

Dynamical CPA and Tight-Binding LMTO Approach to Correlated Electron System

Yoshiro KAKEHASHI*, Takafumi SHIMABUKURO, Toshihito TAMASHIRO,
and Tetsuro NAKAMURA

*Department of Physics and Earth Sciences, Faculty of Science, University of Ryukyus,
1 Senbaru, Nishihara, Okinawa, 903-0213, Japan*

Dynamical Coherent-Potential Approximation (CPA) to correlated electrons has been extended to a system with realistic Hamiltonian which consists of the first-principles tight-binding Linear Muffintin Orbital (LMTO) bands and intraatomic Coulomb interactions. Thermodynamic potential and self-consistent equations for Green function are obtained on the basis of the functional integral method and the harmonic approximation which neglects the mode-mode couplings between the dynamical potentials with different frequency. Numerical calculations have been performed for Fe and Ni within the 2nd-order dynamical corrections to the static approximation. The band narrowing of the quasiparticle states and the 6 eV satellite are obtained for Ni at finite temperatures. The theory leads to the Curie-Weiss law for both Fe and Ni. Calculated effective Bohr magneton numbers are $3.0 \mu_B$ for Fe and $1.2 \mu_B$ for Ni, explaining the experimental data. But calculated Curie temperatures are 2020 K for Fe and 1260 K for Ni, being still overestimated by a factor of two as compared with the experimental ones. Dynamical effects on electronic and magnetic properties are discussed by comparing with those in the static approximations.

KEYWORDS: dynamical CPA, correlated electrons, tight-binding Linear Muffintin Orbital method, iron, nickel, Curie temperature, effective Bohr magneton number, quasiparticle states

1. Introduction

Understanding of electronic and magnetic properties of the system with intermediate strength of Coulomb interactions has been a challenging problem over half a century in condensed matter physics, because simple theoretical approaches are not applicable to the system in spite of the fact that many intriguing phenomena are found there.¹⁻⁴ Iron and nickel are considered to be an example of such systems. These metals in fact show the properties of both the weakly- and the strongly- correlated electrons. Photoemission data, for example, show the existence of metallic *d* bands^{5,6} and the Sommerfeld coefficients in the *T*-linear specific heats show rather large values (5-7 mJ/K²mol) as compared with those of the noble metal systems.⁷ The quasiparticle band widths however are found to be narrower than the results of usual band calculations and a satellite peak is observed at 6 eV below the Fermi level in Ni,⁸ which are not able to be explained by a simple band theory,⁹ suggesting rather strong electron correlations in these systems. The same features are found in the magnetic properties. Noninteger values of the ground-state magnetization in Fe and Ni are well explained by the band theory,¹⁰ while the paramagnetic susceptibilities of these systems follow the Curie-Weiss law and their effective Bohr magneton numbers are close to those expected from the local-moment model.⁷ Large specific heats near the Curie temperature T_C are also well explained by the same model.

The magnetic and electronic properties in the intermediate regime of Coulomb interactions have been traditionally explained by interpolation theories between

the weak and strong Coulomb interaction limits. Cyrot¹¹ proposed an interpolation theory on the basis of the functional integral method which transforms an interacting electron system into an independent electron system with time-dependent random charge and exchange fields. He showed that the static and saddle-point approximations to the functional integral scheme can explain the local-moment vs. itinerant behavior in magnetism of transition metals, as well as the metal-insulator transition.

Hubbard¹² and Hasegawa¹³ independently developed a single-site spin fluctuation theory. They adopted a high temperature approximation (*i.e.*, the static approximation), and treated the random charge and exchange potentials by making use of the coherent potential approximation (CPA). The theory qualitatively described the magnetization vs. temperature curves, the Curie temperature, as well as the Curie-Weiss susceptibility in Fe and Ni. The theory, however, reduces to the Hartree-Fock approximation at zero temperature because it relies on the static approximation. This means that the theory does not take into account the ground-state electron correlations as discussed by Gutzwiller,¹⁴ Hubbard,¹⁵ and Kanamori.¹⁶ Furthermore, the quasiparticle bands and the satellite peak do not appear in the theory using the static approximation.

We proposed the dynamical CPA which fully takes into account the electron correlations within the single-site approximation, and clarified the qualitative features of dynamical effects using a Monte-Carlo sampling method.¹⁷ More recently, we developed analytic method to the dynamical CPA,¹⁸ adopting the harmonic approximation (HA).¹⁹ The latter is based on the neglect of the mode-mode couplings between dynamical potentials in solving an impurity problem in an effective medium.

*E-mail address: yok@sci.u-ryukyu.ac.jp, to be published in Phys. Soc. Jpn. **77** No.9 (2008)

The HA interpolates between the weak Coulomb interaction limit and the atomic limit. Especially it describes the Kondo behavior quantitatively in the strong correlation limit.²⁰ We showed within the single band model that the dynamical CPA+HA yields the band narrowing of quasiparticle states and the satellite peak in Fe and Ni, which were not explained by the early theories with use of the static approximation. The theory was however based on the single-band Hubbard model. Quantitative calculations of transition metals and alloys with use of the realistic Hamiltonian has not yet been made even within the single-site approximation.

In the present paper, we extend the dynamical CPA to the multi-band case adopting the first-principles tight-binding (TB) linear muffintin orbitals (LMTO) method.^{21,22} The modern band theory is based on the density functional theory (DFT) which allows us to express the ground-state energy as a functional of the spin and charge densities of the system.²³ In the local density approximation (LDA),²⁴ one approximates the energy functional with the energy function of the density. The LDA exchange-correlation potentials obtained from the electron gas system have much simplified the electronic band-structure calculations in solids. The TB-LMTO method allows us to construct the first-principles tight-binding one electron Hamiltonian, and to calculate the LDA band structure. We adopt the TB-LMTO Hamiltonian to describe the noninteracting part of the Hamiltonian, and take into account the intraatomic Coulomb and exchange interactions between d electrons which are dominant among electron-electron interactions.

Similar theoretical approach has been developed in the problem of the metal-insulator transition in infinite dimensions.²⁵ The approach called the dynamical mean field theory (DMFT) is equivalent to the dynamical CPA, as we have shown recently.²⁶ The present theory therefore should be equivalent in principle to the DMFT combined with the LDA+U scheme in the band theory.²⁷ The merits of the present approach may be summarized as follows. (1) The dynamical CPA can treat the transverse spin fluctuations for arbitrary d electron number at finite temperatures, while the standard DMFT combined with the quantum Monte-Carlo method (QMC) cannot treat them because it is based on the Ising-type Hubbard-Stratonovich transformation.²⁸ Because of the reason, the DMFT calculations for Fe and Ni have been performed so far without taking into account the transverse spin fluctuations at finite temperatures.²⁹ (2) The HA which we adopted to solve the impurity problem is an analytic approach from the high-temperature limit. The approach is suitable for understanding the finite-temperature magnetism because the zero-th approximation to the HA describes the magnetic properties much better than the Hartree-Fock one. There is no corresponding approach in the DMFT. (3) Because of the analytic theory, we can calculate the excitation spectra up to the temperatures much lower than those calculated by the QMC, using the Padé numerical analytic continuation method.³⁰

In the following section, we introduce a TB-LMTO Hamiltonian with intraatomic Coulomb interactions. In

§3, we formulate the dynamical CPA to the realistic Hamiltonian on the basis of the functional integral technique.³¹ Applying a generalized Hubbard-Stratonovich transformation³² to the free energy, we transform the interacting electrons into an independent electron system with time dependent random fields. Introducing an effective medium into the time dependent Hamiltonian, we will make a single-site approximation. We determine the medium solving a self-consistent equation, called the CPA equation.³³ In §4, we adopt the HA to calculate the dynamical part of the free energy, and derive the analytic expressions of the free energy, the dynamical CPA equation, and other thermodynamic quantities. In §5, we present the numerical results of calculation for Fe and Ni. The calculations have been performed by using the second-order dynamical CPA (*i.e.*, the dynamical CPA+HA within the second-order dynamical corrections). We explain the band narrowing of the quasiparticle states, the incoherent satellite peak at 6 eV below the Fermi level in Ni. We also present the results of calculations for the magnetization vs. temperature curve, the paramagnetic susceptibility following the Curie-Weiss law, and the amplitude of local moments. We clarify the quantitative aspects of the theory comparing with the experimental data, and examine the dynamical effects on various quantities comparing the dynamical results with those in the static approximation. The last section 6 is devoted to summarize the dynamical CPA and TB-LMTO Hamiltonian approach, as well as the dynamical effects in Fe and Ni.

2. TB-LMTO Hamiltonian

We adopt in the present paper the first-principles TB-LMTO method²² to construct a realistic many-body Hamiltonian. In this case, atomic basis function with orbital L on site i , $\chi_{iL}(\mathbf{r} - \mathbf{R}_i)$, are constructed from a muffintin atomic orbital $\varphi_{iL}(\mathbf{r} - \mathbf{R}_i)$ on site i with an atomic level E_{viL} , and a tail function outside the muffintin potential $h_{jL'iL}^\alpha$ as

$$\chi_{iL}(\mathbf{r} - \mathbf{R}_i) = \varphi_{iL}(\mathbf{r} - \mathbf{R}_i) + \sum_{jL'} \dot{\varphi}_{jL'}^\alpha(\mathbf{r} - \mathbf{R}_j) h_{jL'iL}^\alpha, \quad (1)$$

$$\dot{\varphi}_{iL}^\alpha(\mathbf{r} - \mathbf{R}_i) = \dot{\varphi}_{iL}(\mathbf{r} - \mathbf{R}_i) + \varphi_{iL}(\mathbf{r} - \mathbf{R}_i) o_{iL}^\alpha. \quad (2)$$

Here the wave function in the interstitial region has been neglected because of the atomic sphere approximation. The atomic wave function $\varphi_{iL}(\mathbf{r} - \mathbf{R}_i)$ and its energy derivative $\dot{\varphi}_{iL}(\mathbf{r})$ are defined by $\varphi_{iL}(\mathbf{r}) = \phi_{iL}(E_{viL}, r) Y_L(\hat{\mathbf{r}})$ and $\dot{\varphi}_{iL}(\mathbf{r}) = \dot{\phi}_{iL}(E_{viL}, r) Y_L(\hat{\mathbf{r}})$, where $Y_L(\hat{\mathbf{r}})$ is the cubic harmonics with $L = (l, m)$, l being the azimuthal quantum number and m being an orbital index for l . $\phi_{iL}(E, r)$ is obtained by solving the radial Schrödinger equation with energy E . The energy E_{viL} is chosen to be the center of gravity below the Fermi level for each orbital. The atomic orbitals $\{\varphi_{iL}\}$ are normalized in the atomic sphere as $\langle \varphi_{iL} | \varphi_{iL'} \rangle = \delta_{LL'}$. The tail coefficients $h_{jL'iL}^\alpha$ in eq. (1) are determined in such a way that the orbital χ_{iL} is continuous and differentiable

on the sphere boundary at each sphere. The coefficient α_{iL} in eq. (2) is determined so that the orbital χ_{iL} is well localized. We adopt here the nearly orthogonal representation (*i.e.* $\alpha_{iL}^0 = 0$), in which the orbitals χ_{iL} 's become orthogonal up to second order in $h_{iLjL'}$. The TB-LMTO Hamiltonian matrix is then written as

$$\begin{aligned} H_{iLjL'} &= \langle \chi_{iL} | (-\nabla^2 + v(\mathbf{r})) | \chi_{jL'} \rangle \\ &= \epsilon_{iL} \delta_{ij} \delta_{LL'} + t_{iLjL'}. \end{aligned} \quad (3)$$

Here $v(\mathbf{r})$ is a LDA potential, ϵ_{iL} is an atomic level, and $t_{iLjL'}$ is a transfer integral between orbitals χ_{iL} and $\chi_{jL'}$.

When we adopt the density functional theory, the one-electron Hamiltonian (3), especially the atomic level ϵ_{iL} , contains the effects of strong intratomic Coulomb interactions in general. According to the LDA+U interpretation by Anisimov *et al.*,³⁴ the atomic level ϵ_{iL}^0 for non-interacting system is obtained from the relation,

$$\epsilon_{iL}^0 = \frac{\partial E_{\text{LDA}}}{\partial n_{iL\sigma}} - \frac{\partial E_{\text{LDA}}^{\text{U}}}{\partial n_{iL\sigma}}. \quad (4)$$

Here $n_{iL\sigma}$ is the charge density at the ground state, E_{LDA} is the ground-state energy in the LDA, and $E_{\text{LDA}}^{\text{U}}$ is a LDA functional to the intraatomic Coulomb interactions. Among various forms of $E_{\text{LDA}}^{\text{U}}$, we adopt the Hartree-Fock type form³⁵ since we consider here an itinerant electron system where the ratio of the Coulomb interaction to the d band width is not larger than one.

$$\begin{aligned} E_{\text{LDA}}^{\text{U}} &= \frac{1}{2} \sum_j \sum_{mm'\sigma} \bar{U} n_{jd} n_{jd} \\ &\quad + \frac{1}{2} \sum_j \sum_{mm'}' \sum_{\sigma} (\bar{U} - \bar{J}) n_{jd} n_{jd}. \end{aligned} \quad (5)$$

Here $n_{jd} = \sum_{m\sigma} n_{jlm\sigma} / 2(2l+1)$ with $l = 2$. \bar{U} and \bar{J} are the orbital-averaged Coulomb and exchange interactions defined by

$$\bar{U} = \frac{1}{(2l+1)^2} \sum_{mm'} U_{mm'}, \quad (6)$$

$$(\bar{U} - \bar{J}) = \frac{1}{2l(2l+1)} \sum_{mm'}' (U_{mm'} - J_{mm'}), \quad (7)$$

where $U_{mm'}$ and $J_{mm'}$ are orbital dependent intraatomic Coulomb and exchange integrals for d electrons. From eqs. (4) and (5), we obtain the atomic level ϵ_{iL}^0 for non-interacting system as

$$\begin{aligned} \epsilon_{iL}^0 &= \epsilon_{iL} - \left[\left(1 - \frac{1}{2(2l+1)} \right) \bar{U} \right. \\ &\quad \left. - \frac{1}{2} \left(1 - \frac{1}{(2l+1)} \right) \bar{J} \right] n_d \delta_{l2}. \end{aligned} \quad (8)$$

Note that n_d denotes the total d electron number per atom.

The Hamiltonian which we consider here can be written as

$$\hat{H} = H_0 + H_1. \quad (9)$$

The tight-binding Hamiltonian for noninteracting system

H_0 is given by

$$H_0 = \sum_{iL\sigma} (\epsilon_{iL}^0 - \mu) \hat{n}_{iL\sigma} + \sum_{iLjL'\sigma} t_{iLjL'} a_{iL\sigma}^\dagger a_{jL'\sigma}. \quad (10)$$

Here we have introduced the chemical potential μ for the calculation of the free energy. $a_{iL\sigma}^\dagger$ ($a_{iL\sigma}$) is the creation (annihilation) operator for an electron with orbital L and spin σ on site i , and $\hat{n}_{iL\sigma} = a_{iL\sigma}^\dagger a_{iL\sigma}$ is a charge density operator for electrons with orbital L and spin σ on site i . We have neglected the change of the transfer integrals due to electron-electron interactions.

The interacting part H_1 in eq. (9) consists of the intraatomic Coulomb interactions between d electrons.

$$\begin{aligned} H_1 &= \sum_i \left[\sum_m U_0 \hat{n}_{ilm\uparrow} \hat{n}_{ilm\downarrow} \right. \\ &\quad \left. + \sum_{m>m'} (U_1 - \frac{1}{2}J) \hat{n}_{ilm} \hat{n}_{ilm'} - \sum_{m>m'} J \hat{s}_{ilm} \cdot \hat{s}_{ilm'} \right]. \end{aligned} \quad (11)$$

Here U_0 (U_1) and J are the intra-orbital (inter-orbital) Coulomb interaction and the exchange interaction, respectively. \hat{n}_{ilm} (\hat{s}_{ilm}) with $l = 2$ is the charge (spin) density operator for d electrons on site i and orbital m , which is defined by $\hat{n}_{ilm} = \sum_{\sigma} \hat{n}_{ilm\sigma}$ ($\hat{s}_{ilm} = \sum_{\alpha\gamma} a_{iL\alpha}^\dagger (\boldsymbol{\sigma}/2)_{\alpha\gamma} a_{iL\gamma}$), $\boldsymbol{\sigma}$ being the Pauli spin matrices.

3. Functional Integral Approach and Dynamical CPA

Thermodynamic properties of the system are calculated from the partition function, which is given by

$$Z = \text{Tr} \left[\mathcal{T} \exp \left(- \int_0^\beta (H_0(\tau) + H_1(\tau)) d\tau \right) \right]. \quad (12)$$

Here β is the inverse temperature, \mathcal{T} denotes the time-ordered product (T -product) for operators. $H_0(\tau)$ ($H_1(\tau)$) is the interaction representation of Hamiltonian H_0 (H_1).

The functional integral method is based on a Gaussian formula for the Bose-type operators $\{a_\mu\}$.

$$\begin{aligned} \sum_{e \text{ } mm'} a_m A_{mm'} a_{m'} &= \sqrt{\frac{\det A}{\pi^M}} \int \left[\prod_m dx_m \right] \\ &\quad - \sum_{e \text{ } mm'} (x_m A_{mm'} x_{m'} - 2a_m A_{mm'} x_{m'}) \end{aligned} \quad (13)$$

Here $A_{mm'}$ is a $M \times M$ matrix, and $\{x_m\}$ are auxiliary field variables. Discretizing the integral with respect to time in eq. (12), and applying the formula (13) to the Bose-type operators at each time under the T -product, we obtain a functional integral form of the free energy \mathcal{F} as

$$e^{-\beta \mathcal{F}} = \int \left[\prod_{i=1}^N \prod_{m=1}^{2l+1} \delta \boldsymbol{\xi}_{im}(\tau) \delta \zeta_{im}(\tau) \right] Z^0(\boldsymbol{\xi}(\tau), \zeta(\tau))$$

$$\times \exp \left[-\frac{1}{4} \sum_i \sum_{mm'}' \int_0^\beta d\tau \left(\zeta_{im}(\tau) A_{imm'} \zeta_{m'}(\tau) + \sum_{\alpha}^{xyz} \xi_{im\alpha}(\tau) B_{imm'}^\alpha \xi_{im'\alpha}(\tau) \right) \right], \quad (14)$$

$$Z^0(\xi(\tau), \zeta(\tau)) = \text{Tr} \left(T \exp \left[-\int_0^\beta H(\tau, \xi, -i\zeta) d\tau \right] \right), \quad (15)$$

$$H(\tau, \xi, -i\zeta) = \sum_{iL} \left[\left(\epsilon_{iL}^0 - \mu - \frac{1}{2} \sum_{m'} i A_{imm'} \zeta_{im'}(\tau) \delta_{l2} \right) \hat{n}_{iL}(\tau) - \sum_{\alpha} \left(\frac{1}{2} \sum_{m'} B_{imm'}^\alpha \xi_{im'\alpha}(\tau) + h_{im}^\alpha \right) \delta_{l2} \hat{m}_{iL}^\alpha(\tau) \right] + \sum_{iLjL'\sigma} t_{iLjL'} a_{iL\sigma}^\dagger(\tau) a_{jL'\sigma}(\tau). \quad (16)$$

Here N is the number of sites, $\hat{\mathbf{m}}_{iL} = 2\hat{\mathbf{s}}_{iL}$, and $\zeta_{im}(\tau)$ ($\xi_{im}(\tau)$) is an auxiliary field being conjugate with $i\hat{n}_{iL}(\tau)$ ($\hat{\mathbf{m}}_{iL}(\tau)$) for $l = 2$. The functional integrals in eq. (14) are, for example, defined by

$$\int \left[\prod_{n=1}^{2l+1} \delta \zeta_{im}(\tau) \right] = \int \left[\prod_{n=1}^{N'} \sqrt{\frac{\beta^{2l+1} \det A_i}{(4\pi)^{2l+1}}} \frac{d\zeta_{im}(\tau_n)}{\sqrt{N'}} \right], \quad (17)$$

where $2l+1$ in the square roots denotes the number of d orbitals (*i.e.*, $2l+1 = 5$). $\det A_i$ is the determinant of the $(2l+1) \times (2l+1)$ matrix $A_{imm'}$. τ_n denotes the n -th time when the time interval $[0, \beta]$ is divided into N' segments. The matrices $A_{imm'}$ and $B_{imm'}^\alpha$ ($\alpha = x, y, z$) are defined as

$$A_{imm'} = U_0 \delta_{mm'} + (2U_1 - J)(1 - \delta_{mm'}), \quad (18)$$

$$B_{imm'}^\alpha = J(1 - \delta_{mm'}), \quad (\alpha = x, y), \quad (19)$$

$$B_{imm'}^z = U_0 \delta_{mm'} + J(1 - \delta_{mm'}). \quad (20)$$

Equation (15) is a partition function for a time-dependent Hamiltonian $H(\tau, \xi, -i\zeta)$ of an independent particle system. Note that we have introduced a magnetic field h_{im}^α for convenience.

In the Matsubara frequency representation, the free energy \mathcal{F} is written as

$$e^{-\beta\mathcal{F}} = \int \left[\prod_{j=1}^N \prod_{m=1}^{2l+1} \delta \xi_{jm} \delta \zeta_{jm} \right] \exp[-\beta E[\xi, \zeta]], \quad (21)$$

$$E[\xi, \zeta] = -\beta^{-1} \ln \text{Tr}(e^{-\beta H_0}) - \beta^{-1} \text{Sp} \ln(1 - vg) + \frac{1}{4} \sum_{in} \sum_{mm'} \left[\zeta_{im}^*(i\omega_n) A_{imm'} \zeta_{m'}(i\omega_n) + \sum_{\alpha} \xi_{im\alpha}^*(i\omega_n) B_{imm'}^\alpha \xi_{im'\alpha}(i\omega_n) \right], \quad (22)$$

$$(v)_{iLn\sigma jL'n'\sigma'} = v_{jL\sigma\sigma'}(i\omega_n - i\omega_{n'}) \delta_{ij} \delta_{LL'}, \quad (23)$$

$$v_{iL\sigma\sigma'}(i\omega_n) = -\frac{1}{2} \sum_{m'} i A_{imm'} \zeta_{im'}(i\omega_n) \delta_{l2} \delta_{\sigma\sigma'}$$

$$- \sum_{\alpha} \left(\frac{1}{2} \sum_{m'} B_{imm'}^\alpha \xi_{im'\alpha}(i\omega_n) + h_{im}^\alpha \right) \delta_{l2} (\sigma_\alpha)_{\sigma\sigma'}. \quad (24)$$

The functional integrals in the Fourier representation in eq. (21) is given by

$$\int \left[\prod_{m=1}^{2l+1} \delta \zeta_{im} \right] = \int \prod_{m=1}^{N'} \sqrt{\frac{\beta^{2l+1} \det A_i}{(4\pi)^{2l+1}}} \prod_{m=1}^{2l+1} d\zeta_{im}(0) \times \left[\prod_{n=1}^{\infty} \frac{\beta^{2l+1} \det A_i}{(4\pi)^{2l+1}} d^2 \zeta_{im}(i\omega_n) \right]. \quad (25)$$

Here the field variable $\zeta_{im}(i\omega_n)$ ($\xi_{im\alpha}(i\omega_n)$) denotes the n -frequency component of $\zeta_{im}(\tau)$ ($\xi_{im\alpha}(\tau)$), and $d^2 \zeta_{im}(i\omega_n) = d\text{Re} \zeta_{im}(i\omega_n) d\text{Im} \zeta_{im}(i\omega_n)$. The energy functional $E[\xi, \zeta]$ in eq. (22) consists of the noninteracting term (the first term at the r.h.s. (the right-hand-side)), the scattering term due to dynamical potential (the second term), and the Gaussian term (the third term). Sp in the second term at the r.h.s. of eq. (22) means a trace over site, orbital, frequency, and spin. g in the second term denotes the temperature Green function for noninteracting system H_0 . The dynamical potential v is defined by eqs. (23) and (24), and σ_α in eq. (24) denotes the α component of the Pauli spin matrices.

In the effective medium approach,¹⁸ we introduce a coherent potential

$$(\Sigma)_{iLn\sigma jL'n'\sigma'} = \Sigma_{L\sigma}(i\omega_n) \delta_{ij} \delta_{LL'} \delta_{nn'} \delta_{\sigma\sigma'}, \quad (26)$$

into the energy functional $E[\xi, \zeta]$, and expand it with respect to $v - \Sigma$ as

$$E[\xi, \zeta] = \tilde{\mathcal{F}} + \sum_i E_i[\xi_i, \zeta_i] + \Delta E. \quad (27)$$

Here the zero-th order term $\tilde{\mathcal{F}}$ is a coherent part of the free energy which is defined by

$$\tilde{\mathcal{F}} = -\beta^{-1} \ln \text{Tr}(e^{-\beta H_0}) - \beta^{-1} \text{Sp} \ln(1 - \Sigma g). \quad (28)$$

Note that the coherent part does not depend on the dynamical potential.

The next term in eq. (27) consists of a sum of the single-site energies $E_i[\xi_i, \zeta_i]$, which are defined by

$$E_i[\xi_i, \zeta_i] = -\beta^{-1} \text{tr} \ln(1 - \delta v_i F_i) + \frac{1}{4} \sum_n \sum_{mm'} [\zeta_{im}^*(i\omega_n) A_{imm'} \zeta_{m'}(i\omega_n) + \sum_{\alpha}^{xyz} \xi_{im\alpha}^*(i\omega_n) B_{imm'}^\alpha \xi_{im'\alpha}(i\omega_n)]. \quad (29)$$

Here tr means a trace over orbital, frequency, and spin on site i . $\delta v_i = v_i - \Sigma_i$, and v_i (Σ_i) is the dynamical (coherent) potential on site i . F_i is the site-diagonal component of the coherent Green function defined by

$$(F_i)_{jLn\sigma j'L'n'\sigma'} = F_{iL\sigma}(i\omega_n) \delta_{ij} \delta_{ij'} \delta_{LL'} \delta_{nn'} \delta_{\sigma\sigma'}, \quad (30)$$

$$F_{iL\sigma}(i\omega_n) = [(g^{-1} - \Sigma)^{-1}]_{iLn\sigma iLn\sigma}. \quad (31)$$

The last term in eq. (27) denotes the higher order terms in expansion.

$$\Delta E = -\beta^{-1} \text{Sp} \ln(1 - \tilde{t} F'). \quad (32)$$

Here \tilde{t} is the single-site t -matrix defined by

$$\tilde{t} = (1 - \delta v_i F_i)^{-1} \delta v_i, \quad (33)$$

and F' is the off-diagonal coherent Green Function defined by

$$(F')_{iLn\sigma jL'n'\sigma'} = [(g^{-1} - \Sigma)^{-1}]_{iLn\sigma jL'n'\sigma'} (1 - \delta_{ij}) \delta_{\sigma\sigma'}. \quad (34)$$

The dynamical CPA is a single-site approximation which neglects the intersite dynamical correlations ΔE . The free energy is then written as

$$\mathcal{F}_{\text{CPA}} = \tilde{\mathcal{F}} - \sum_i \beta^{-1} \ln \int [\prod_m \delta \xi_{im} \delta \zeta_{im}] e^{-\beta E_i[\xi_i, \zeta_i]}. \quad (35)$$

The dynamical coherent potential $\Sigma_{iL\sigma}(i\omega_n)$ should be determined so that the nonlocal corrections ΔE vanish in average. This means that

$$\langle \tilde{t}_i \rangle = 0, \quad (36)$$

where

$$\langle (\sim) \rangle = \frac{\int [\prod_m \delta \xi_{im} \delta \zeta_{im}] (\sim) e^{-\beta E_i[\xi_i, \zeta_i]}}{\int [\prod_m \delta \xi_{im} \delta \zeta_{im}] e^{-\beta E_i[\xi_i, \zeta_i]}}. \quad (37)$$

The above condition called the CPA equation is written as

$$\langle G_{iL\sigma}^{(i)}(i\omega_n) \rangle = F_{iL\sigma}(i\omega_n), \quad (38)$$

$$G_{iL\sigma}^{(i)}(i\omega_n) = [(F_i^{-1} - \delta v_i)^{-1}]_{iLn\sigma iLn\sigma}. \quad (39)$$

Here the l.h.s. (left-hand-side) of eq. (38) is a temperature Green function for an impurity system in the effective medium, whose Hamiltonian is given as follows.

$$H^{(i)}(\tau) = \tilde{H}(\tau) + H_1^{(i)}(\tau) - \int_0^\beta d\tau' \sum_{L\sigma} a_{iL\sigma}^\dagger(\tau) \Sigma_{iL\sigma}(\tau - \tau') a_{jL\sigma}(\tau'), \quad (40)$$

$$\begin{aligned} \tilde{H}(\tau) &= \sum_{iL\sigma} (\epsilon_{iL}^0 - \mu) \hat{n}_{iL\sigma}(\tau) \\ &+ \sum_{iLjL'\sigma} t_{iLjL'} a_{iL\sigma}^\dagger(\tau) a_{jL'\sigma}(\tau) \\ &+ \sum_{jL\sigma} \int_0^\beta d\tau' a_{jL\sigma}^\dagger(\tau) \Sigma_{jL\sigma}(\tau - \tau') a_{jL\sigma}(\tau'), \end{aligned} \quad (41)$$

$$\begin{aligned} H_1^{(i)}(\tau) &= \sum_m U_0 \hat{n}_{ilm\uparrow}(\tau) \hat{n}_{ilm\downarrow}(\tau) \\ &+ \sum_{m>m'} (U_1 - \frac{1}{2}J) \hat{n}_{ilm}(\tau) \hat{n}_{ilm'}(\tau) \\ &- \sum_{m>m'} J \hat{s}_{ilm}(\tau) \cdot \hat{s}_{ilm'}(\tau). \end{aligned} \quad (42)$$

It should be noted that the CPA equation (38) is equivalent to the following stationary condition.

$$\frac{\delta \mathcal{F}_{\text{CPA}}}{\delta \Sigma_{iL\sigma}(i\omega_n)} = 0. \quad (43)$$

4. Harmonic Approximation to the Dynamical CPA

We can rewrite the free energy (35) by means of an effective potential projected onto the zero frequency variables $\xi_{im} = \xi_{im}(0)$ and $\zeta_{im} = \zeta_{im}(0)$.

$$\begin{aligned} \mathcal{F}_{\text{CPA}} &= \tilde{\mathcal{F}} \\ &- \beta^{-1} \ln \int \left[\prod_\alpha \sqrt{\frac{\beta^{2l+1} \det B^\alpha}{(4\pi)^{2l+1}}} \prod_m d\xi_{m\alpha} \right] \\ &\times \sqrt{\frac{\beta^{2l+1} \det A}{(4\pi)^{2l+1}}} \left[\prod_m d\zeta_m \right] e^{-\beta E(\xi, \zeta)}. \end{aligned} \quad (44)$$

Note that we have redefined \mathcal{F}_{CPA} and \mathcal{F} by those per site, assuming that all the sites are equivalent to each other. Furthermore we omit here and in the following all the site indices for simplicity.

The effective potential $E(\xi, \zeta)$ in eq. (44) consists of the static part $E_{\text{st}}(\xi, \zeta)$ and the dynamical one $E_{\text{dyn}}(\xi, \zeta)$.

$$E(\xi, \zeta) = E_{\text{st}}(\xi, \zeta) + E_{\text{dyn}}(\xi, \zeta), \quad (45)$$

$$\begin{aligned} E_{\text{st}}(\xi, \zeta) &= -\beta^{-1} \text{tr} \ln [1 - \delta v_0 F_i] \\ &+ \frac{1}{4} \sum_{mm'} [\zeta_m A_{mm'} \zeta_{m'} + \sum_\alpha \xi_{m\alpha} B_{mm'}^\alpha \xi_{im'\alpha}], \end{aligned} \quad (46)$$

$$\begin{aligned} e^{-\beta E_{\text{dyn}}(\xi, \zeta)} &= \overline{D} \\ &\equiv \int \prod_{n=1}^\infty \left[\prod_\alpha \frac{\beta^{2l+1} \det B^\alpha}{(2\pi)^{2l+1}} d^2 \xi_{m\alpha}(i\omega_n) \right] \frac{\beta^{2l+1} \det A}{(2\pi)^{2l+1}} \left[\prod_m d^2 \zeta_m(i\omega_n) \right] \\ &\times D \exp \left[-\frac{\beta}{4} \sum_{n \neq 0} \sum_{mm'} (\zeta_m^*(i\omega_n) A_{mm'} \zeta_{m'}(i\omega_n) \right. \\ &\quad \left. + \sum_\alpha \xi_{m\alpha}^*(i\omega_n) B_{mm'}^\alpha \xi_{m'\alpha}(i\omega_n) \right], \end{aligned} \quad (47)$$

$$\begin{aligned} D &= \det \left(\delta_{nn'} \delta_{LL'} \delta_{\sigma\sigma'} \right. \\ &\quad \left. - \sum_{\sigma''} \tilde{v}_{L\sigma\sigma''}(i\omega_n - i\omega_{n'}) \tilde{g}_{L\sigma''L'\sigma'}(i\omega_{n'}) \right). \end{aligned} \quad (48)$$

Here δv_0 in eq. (46) is defined by $\delta v_0 = v(0) - \Sigma$:

$$(\delta v_0)_{Ln\sigma L'n'\sigma'} = (v_{L\sigma\sigma'}(0) - \Sigma_{L\sigma}(i\omega_n) \delta_{\sigma\sigma'}) \delta_{LL'} \delta_{nn'}. \quad (49)$$

$v_{L\sigma\sigma'}(0)$ is the static potential, while \tilde{v} in eq. (48) is the dynamical potential without zero frequency part.

$$\tilde{v}_{L\sigma\sigma'}(i\omega_n - i\omega_{n'}) = v_{L\sigma\sigma'}(i\omega_n - i\omega_{n'}) - v_{L\sigma\sigma'}(0) \delta_{nn'}. \quad (50)$$

Furthermore, $\tilde{g}_{L\sigma L'\sigma'}(i\omega_n)$ in eq. (48) is the Green function in the static approximation defined by

$$\tilde{g}_{L\sigma L'\sigma'}(i\omega_n) = [(F^{-1} - \delta v_0)^{-1}]_{Ln\sigma L'n'\sigma'}, \quad (51)$$

where the coherent Green function F is defined by eqs. (30) and (31).

In the functional integral approach, we first have to calculate the determinant (48), and second have to eval-

uate the functional integral in eq. (47). In order to implement these calculations, we expand the determinant (48) with respect to the frequency modes of the dynamical potential $v_{L\sigma\sigma'}$ as follows.

$$D = 1 + \sum_{\nu} (D_{\nu} - 1) + \sum_{(\nu, \nu')} (D_{\nu\nu'} - D_{\nu} - D_{\nu'} + 1) + \cdots, \quad (52)$$

$$D_{\nu} = \det \left[\delta_{LL'} \delta_{\sigma\sigma'} \delta_{nn'} - \sum_{\sigma''} (v_{L\sigma\sigma''}(\omega_{\nu}) \delta_{n-n', \nu} + v_{L\sigma\sigma''}(\omega_{-\nu}) \delta_{n-n', -\nu}) \tilde{g}_{L\sigma''L'\sigma'}(\omega_{n'}) \right], \quad (53)$$

$$D_{\nu\nu'} = \det \left[\delta_{LL'} \delta_{\sigma\sigma'} \delta_{nn'} - \sum_{\sigma''} (v_{L\sigma\sigma''}(\omega_{\nu}) \delta_{n-n', \nu} + v_{L\sigma\sigma''}(\omega_{-\nu}) \delta_{n-n', -\nu}) \tilde{g}_{L\sigma''L'\sigma'}(\omega_{n'}) - \sum_{\sigma''} (v_{L\sigma\sigma''}(\omega_{\nu'}) \delta_{n-n', \nu'} + v_{L\sigma\sigma''}(\omega_{-\nu'}) \delta_{n-n', -\nu'}) \tilde{g}_{L\sigma''L'\sigma'}(\omega_{n'}) \right]. \quad (54)$$

The first term at the r.h.s. of eq. (52) corresponds to the zero-th approximation (*i.e.* the static approximation) which neglects dynamical potentials. The second term is a superposition of the independent scattering terms of dynamical potential $v_{L\sigma\sigma'}(\omega_{\nu})$. Higher order terms describe dynamical mode-mode couplings.

We adopt here the harmonic approximation¹⁹ which neglects the mode-mode coupling terms in eq. (52). We have then

$$E_{\text{dyn}}(\xi, \zeta) = -\beta^{-1} \ln \left[1 + \sum_{\nu} (\overline{D}_{\nu} - 1) \right]. \quad (55)$$

The approximation yields the result of the second-order perturbation in the weak Coulomb interaction limit, and describes the Kondo anomaly in the strong interaction limit.²⁰

Let us now calculate \overline{D}_{ν} in eq. (55). The determinant D_{ν} in the harmonic approximation is written by a product of those of the tridiagonal-type matrices as

$$D_{\nu} = \prod_{k=0}^{\nu-1} \left[\prod_{m=1}^{2l+1} D_{\nu}(k, m) \right], \quad (56)$$

$$D_{\nu}(k, m) = \begin{vmatrix} \ddots & & & & \\ & 1 & 1 & & 0 \\ & a_{-\nu+k}(\nu, m) & 1 & 1 & \\ & & a_k(\nu, m) & 1 & 1 \\ & & & a_{\nu+k}(\nu, m) & 1 & 1 \\ 0 & & & & a_{2\nu+k}(\nu, m) & \\ & & & & & \ddots \end{vmatrix}. \quad (57)$$

Here 1 in the determinant is the 2×2 unit matrix, $a_n(\nu, m)$ is a 2×2 matrix defined by

$$a_n(\nu, m)_{\sigma\sigma'} = \sum_{\sigma''\sigma'''\sigma''''} v_{L\sigma\sigma''}(\nu)$$

$$\times \tilde{g}_{L\sigma''\sigma'''}(n - \nu) v_{L\sigma'''\sigma''''}(-\nu) \tilde{g}_{L\sigma''''\sigma'}(n). \quad (58)$$

We assumed in the above expression that the orbitals $\{L\}$ form an irreducible representation of the point group of the system, so that $\tilde{g}_{L\sigma L'\sigma'}(\omega_n) = \tilde{g}_{L\sigma\sigma'}(\omega_n) \delta_{LL'}$ (see eq. (51)). Furthermore here and in the following, we write the frequency dependence, for example, of $\tilde{g}_{L\sigma\sigma'}(\omega_n)$ as $\tilde{g}_{L\sigma\sigma'}(n)$ for simplicity.

The determinant $D_{\nu}(k, m)$ is expanded with respect to the dynamical potentials as follows.

$$D_{\nu}(k, m) = 1 + D_{\nu}^{(1)}(k, m) + D_{\nu}^{(2)}(k, m) + \cdots, \quad (59)$$

$$D_{\nu}^{(n)}(k, m) = \sum_{\alpha_1 \gamma_1 \cdots \alpha_n \gamma_n} v_{\alpha_1}(\nu, m) v_{\gamma_1}(-\nu, m) \cdots \times v_{\alpha_n}(\nu, m) v_{\gamma_n}(-\nu, m) \hat{D}_{\{\alpha\gamma\}}^{(n)}(\nu, k, m). \quad (60)$$

Here the subscripts α_i and γ_i take 4 values 0, x , y , and z , and

$$v_0(\nu, m) = -\frac{1}{2} i \sum_{m'} A_{mm'} \zeta_{m'}(\nu) \delta_{l2}, \quad (61)$$

$$v_{\alpha}(\nu, m) = -\frac{1}{2} \sum_{m'} B_{mm'}^{\alpha} \xi_{m'\alpha}(\nu) \delta_{l2}, \quad (\alpha = x, y, z). \quad (62)$$

Note that the subscript $\{\alpha\gamma\}$ in eq. (60) denotes a set of $(\alpha_1 \gamma_1 \cdots \alpha_n \gamma_n)$. The expressions of $\hat{D}_{\{\alpha\gamma\}}^{(n)}(\nu, k, m)$ are given in Appendix A.

Substituting eq. (59) into eq. (56) and taking the Gaussian average (47), we have

$$\overline{D}_{\nu} = \sum_{n=0}^{\infty} \sum_{\alpha_1 \gamma_1 \cdots \alpha_n \gamma_n} \sum_{\sum_{km} l(k, m) = n} \overline{\left[\prod_{m=1}^{2l+1} v_{\alpha_i}(\nu, m) v_{\gamma_i}(-\nu, m) \right]} \times \left[\prod_{m=1}^{2l+1} \prod_{k=0}^{\nu-1} \hat{D}_{\{\alpha\gamma\}}^{(l(k, m))}(\nu, k, m) \right]. \quad (63)$$

Here $\{l(k, m)\} (k = 0, \cdots, \nu - 1, m = 1, \cdots, 2l + 1)$ are zero or positive integer, satisfying $\sum_{km} l(k, m) = n$. $\prod_i v_{\alpha_i}(\nu, m) v_{\gamma_i}(-\nu, m)$ are the products of $v_{\alpha_i}(\nu, m) v_{\gamma_i}(-\nu, m)$ belonging to the m -th orbital block. Calculations of the Gaussian average of the dynamical potentials are given in Appendix B, and we reach the following expression.

$$\overline{D}_{\nu} = 1 + \overline{D}_{\nu}^{(1)} + \overline{D}_{\nu}^{(2)} + \cdots, \quad (64)$$

$$\overline{D}_{\nu}^{(n)} = \frac{1}{(2\beta)^n} \sum_{\sum_{km} l(k, m) = n} \sum_{\{\alpha_j(k, m)\}} \sum_P \prod_{m=1}^{2l+1} \prod_{k=0}^{\nu-1} \left[\left(\prod_{j=1}^{l(k, m)} C_{m m_p}^{\alpha_j(k, m)} \right) \hat{D}_{\{\alpha_{p-1}\}}^{(l(k, m))}(\nu, k, m) \right]. \quad (65)$$

Here j denotes the j -th member of the (k, m) block. P denotes a permutation of a set $\{(j, k, m)\}$: $P\{(j, k, m)\} = \{(j_p, k_p, m_p)\}$, α_{p-1} means an rearrangement of $\{\alpha_j(k, m)\}$ according to the inverse permutation P^{-1} . Note that $\alpha_j(k, m)$ takes 4 values 0, x , y , and z .

$C_{mm'}^\alpha$ is a Coulomb interaction defined by

$$C_{mm'}^\alpha = \begin{cases} -A_{mm'} & (\alpha = 0) \\ B_{mm'}^\alpha & (\alpha = x, y, z) \end{cases} \quad (66)$$

Equations (55) and (64) determine the dynamical potential $E_{\text{dyn}}(\xi, \zeta)$.

The free energy (44) is written alternatively as

$$\mathcal{F}_{\text{CPA}} = \tilde{\mathcal{F}} - \beta^{-1} \ln \int \left[\prod_{\alpha} \sqrt{\frac{\beta^{2l+1} \det B^\alpha}{(4\pi)^{2l+1}}} \prod_m d\xi_m \right] \times e^{-\beta E_{\text{eff}}(\xi)} \quad (67)$$

In the itinerant electron system, spin fluctuations plays an important role, and we may neglect the thermal charge fluctuations making use of the saddle-point approximation to the static charge fields ζ_m . We have then $E_{\text{eff}}(\xi) = E(\xi, \zeta^*)$. The saddle point value ζ_m^* is determined from $\partial E(\xi, \zeta^*)/\partial \zeta_m = 0$:

$$-i\zeta_m^* = \tilde{n}_L(\xi) = \sum_{\sigma} \tilde{n}_{L\sigma}(\xi) \quad (68)$$

$$\tilde{n}_{L\sigma}(\xi) = \frac{1}{\beta} \sum_n G_{L\sigma}(n) \quad (69)$$

In order to reduce the number of variables, we neglect the out-of-phase thermal spin fluctuations between different orbitals on a site, and take into account their in-phase fluctuations. This can be made by introducing a large variable $\xi_\alpha = \sum_m \xi_{m\alpha}$. Inserting $1 = \int [\prod_{\alpha} d\xi_{\alpha} d\lambda_{\alpha}] \exp[-2\pi i \lambda_{\alpha} (\xi_{\alpha} - \sum_m \xi_{m\alpha})]$ into eq. (67), and replacing variables $\xi_{m\alpha}$ with $\xi_{\alpha}/(2l+1)$ in the non-Gaussian terms of $E_{\text{eff}}(\xi)$, we reach

$$\mathcal{F}_{\text{CPA}} = \tilde{\mathcal{F}} - \beta^{-1} \ln \int \left[\prod_{\alpha} \sqrt{\frac{\beta \tilde{J}_{\alpha}}{4\pi}} d\xi_{\alpha} \right] e^{-\beta E_{\text{eff}}(\xi)} \quad (70)$$

$$E_{\text{eff}}(\xi) = E_{\text{st}}(\xi) + E_{\text{dyn}}(\xi) \quad (71)$$

$$E_{\text{st}}(\xi) = -\frac{1}{\beta} \sum_{mn} \ln \left[(1 - \delta v_{L\uparrow}(0) F_{L\uparrow}(n)) (1 - \delta v_{L\downarrow}(0) F_{L\downarrow}(n)) \right. \\ \left. - \frac{1}{4} \tilde{J}_{\perp}^2 \xi_{\perp}^2 F_{L\uparrow}(n) F_{L\downarrow}(n) \right] \\ + \frac{1}{4} \left[-(U_0 - 2U_1 + J) \sum_m \tilde{n}_L(\xi)^2 \right. \\ \left. - (2U_1 - J) \tilde{n}_L(\xi)^2 + \tilde{J}_{\perp}^2 \xi_{\perp}^2 + \tilde{J}_z^2 \xi_z^2 \right] \quad (72)$$

Here $\tilde{J}_x = \tilde{J}_y = \tilde{J}_{\perp} = (1 - 1/(2l+1))J$, $\tilde{J}_z = U_0/(2l+1) + \tilde{J}_{\perp}$, $\delta v_{L\sigma}(0) = v_{L\sigma}(0) - \Sigma_{L\sigma}(n)$, and $v_{L\sigma}(0) = v_0(0, m) + \sigma v_z(0, m)$. The charge densities, $\tilde{n}_L(\xi)$ and $\tilde{n}_l(\xi)$ are defined by $\tilde{n}_L(\xi) = \sum_{\sigma} \tilde{n}_{L\sigma}(\xi)$ and $\tilde{n}_l(\xi) = \sum_m \tilde{n}_L(\xi)$. Furthermore $E_{\text{dyn}}(\xi)$ is given by eq. (55) in which ζ_m ($\xi_{m\alpha}$) has been replaced by $i\tilde{n}_L(\xi)$ ($\xi_{\alpha}/(2l+1)$).

The CPA equation in the HA is obtained from the stationary condition (43) with the free energy (70).

$$\langle G_{L\sigma}(n) \rangle = F_{L\sigma}(n) \quad (73)$$

and

$$\langle G_{L\sigma}(n) \rangle = \left\langle \tilde{g}_{L\sigma\sigma}(n) - \frac{\beta}{\kappa_{L\sigma}(n)} \frac{\delta E_{\text{dyn}}}{\delta \Sigma_{L\sigma}(n)} \right\rangle \quad (74)$$

Here $\kappa_{L\sigma}(n) = 1 - F_{L\sigma}(n)^{-2} H_{L\sigma}(n)$ and $H_{L\sigma}(n) = \delta F_{L\sigma}(n)/\delta \Sigma_{L\sigma}(n)$. The average $\langle \sim \rangle$ at the r.h.s. of eq. (74) is now defined by a classical average with respect to the effective potential (71).

$$\langle \sim \rangle = \frac{\int \left[\prod_{\alpha} d\xi_{\alpha} \right] (\sim) e^{-\beta E_{\text{eff}}(\xi)}}{\int \left[\prod_{\alpha} d\xi_{\alpha} \right] e^{-\beta E_{\text{eff}}(\xi)}} \quad (75)$$

Substituting eq. (55) into Eq. (74), we obtain the expression

$$\langle G_{L\sigma}(n) \rangle = \left\langle \tilde{g}_{L\sigma\sigma}(n) - \frac{\sum_{\nu} \frac{\delta \bar{D}_{\nu}}{\kappa_{L\sigma}(n) \delta \Sigma_{L\sigma}(n)}}{1 + \sum_{\nu} (\bar{D}_{\nu} - 1)} \right\rangle \quad (76)$$

The local charge and magnetic moment are obtained from $\partial \mathcal{F}_{\text{CPA}}/\partial \epsilon_L^0$ and $-\partial \mathcal{F}_{\text{CPA}}/\partial h_L^{\alpha}$. Making use of the stationary conditions of \mathcal{F}_{CPA} with respect to ζ_m^* and $\Sigma_{L\sigma}$, and the CPA equation (73), we reach

$$\langle \hat{n}_L \rangle = \frac{1}{\beta} \sum_{n\sigma} F_{L\sigma}(n) \quad (77)$$

$$\langle \hat{m}_L^z \rangle = \frac{1}{\beta} \sum_{n\sigma} \sigma F_{L\sigma}(n) \quad (78)$$

In particular, the $l = 2$ components of local charge and magnetic moment are expressed as

$$\langle \hat{n}_l \rangle = \langle \tilde{n}_l(\xi) \rangle \quad (79)$$

$$\langle \hat{m}_l \rangle = \langle \xi \rangle \quad (80)$$

The amplitude of charge and local moments for d electrons are calculated from the formulae.

$$\langle \hat{n}_l^2 \rangle = \langle \hat{n}_l \rangle + 2 \sum_m \frac{\partial \mathcal{F}_{\text{CPA}}}{\partial U_{mm}} + \sum_{mm'}' \frac{\partial \mathcal{F}_{\text{CPA}}}{\partial U_{mm'}} \quad (81)$$

$$\langle \mathbf{m}_l^2 \rangle = 3 \langle n_l \rangle - 6 \sum_m \frac{\partial \mathcal{F}_{\text{CPA}}}{\partial U_{mm}} \\ - \sum_{mm'}' \left(\frac{\partial \mathcal{F}_{\text{CPA}}}{\partial U_{mm'}} + 2 \frac{\partial \mathcal{F}_{\text{CPA}}}{\partial J_{mm'}} \right) \quad (82)$$

Here we have introduced for convenience orbital-dependent Coulomb and exchange interactions $U_{mm'}$ and $J_{mm'}$ into the interaction H_1 to derive the expressions. Making use of the stationary conditions of \mathcal{F}_{CPA} and integrations by parts, we obtain

$$\langle \hat{n}_l^2 \rangle = \langle \tilde{n}_l(\xi) \rangle + \frac{1}{2} \sum_m \langle \tilde{n}_L(\xi)^2 \rangle + \sum_{mm'}' \langle \tilde{n}_L(\xi) \tilde{n}_{L'}(\xi) \rangle \\ - \frac{1}{2(2l+1)} \left(\langle \xi_z^2 \rangle - \frac{2}{\beta \tilde{J}_z} \right) \\ + 2 \sum_m \left\langle \left[\frac{\partial E_{\text{dyn}}}{\partial U_{mm}} \right]_v \right\rangle + \sum_{mm'}' \left\langle \left[\frac{\partial E_{\text{dyn}}}{\partial U_{mm}} \right]_v \right\rangle \quad (83)$$

$$\begin{aligned}
\langle \hat{m}_l^2 \rangle &= 3\langle \tilde{n}_l(\boldsymbol{\xi}) \rangle - \frac{3}{2} \sum_m \langle \tilde{n}_L(\boldsymbol{\xi})^2 \rangle \\
&\quad + \frac{3}{2(2l+1)} \left(\langle \xi_z^2 \rangle - \frac{2}{\beta \tilde{J}_z} \right) \\
&\quad + \left(1 - \frac{1}{2l+1} \right) \sum_{\alpha=x,y} \left(\langle \xi_\alpha^2 \rangle - \frac{2}{\beta \tilde{J}_\alpha} \right) \\
&\quad - 6 \sum_m \left\langle \left[\frac{\partial E_{\text{dyn}}}{\partial U_{mm'}} \right]_v \right\rangle - \sum_{mm'}' \left(\left\langle \left[\frac{\partial E_{\text{dyn}}}{\partial U_{mm'}} \right]_v \right\rangle \right. \\
&\quad \left. + 2 \left\langle \left[\frac{\partial E_{\text{dyn}}}{\partial J_{mm'}} \right]_v \right\rangle \right). \quad (84)
\end{aligned}$$

Here $[\partial E_{\text{dyn}}/\partial U_{mm'}]_v$ means taking derivative of E_{dyn} with respect to $U_{mm'}$ fixing the static potentials $v_{L\sigma\sigma'}(0)$. In the HA, these values are obtained from eq. (55) as

$$\left[\frac{\partial E_{\text{dyn}}}{\partial U_{mm'}} \right]_v = -\frac{1}{\beta} \frac{\sum_{\nu=1}^{\infty} \left[\frac{\partial \bar{D}_\nu}{\partial U_{mm'}} \right]_v}{1 + \sum_{\nu=1}^{\infty} (\bar{D}_\nu - 1)}, \quad (85)$$

$$\left[\frac{\partial E_{\text{dyn}}}{\partial J_{mm'}} \right]_v = -\frac{1}{\beta} \frac{\sum_{\nu=1}^{\infty} \left[\frac{\partial \bar{D}_\nu}{\partial J_{mm'}} \right]_v}{1 + \sum_{\nu=1}^{\infty} (\bar{D}_\nu - 1)}. \quad (86)$$

The entropy is calculated from $\beta^2 \partial \mathcal{F}_{\text{CPA}} / \partial \beta$ as

$$\begin{aligned}
S &= \beta^2 \frac{\partial \tilde{\mathcal{F}}}{\partial \beta} + \left\langle \beta^2 \frac{\partial E_{\text{eff}}}{\partial \beta} \right\rangle \\
&\quad + \ln \int \left[\prod_\alpha \sqrt{\frac{\beta \tilde{J}_\alpha}{4\pi}} d\xi_\alpha \right] e^{-\beta(E_{\text{eff}}(\boldsymbol{\xi}) - \langle E_{\text{eff}}(\boldsymbol{\xi}) \rangle) - \frac{3}{2}}. \quad (87)
\end{aligned}$$

Here

$$\beta^2 \frac{\partial \tilde{\mathcal{F}}}{\partial \beta} = \frac{1}{N} \text{Sp} \ln (g^{-1} - \Sigma) + \sum_n \sum_{L\sigma} F_{L\sigma}(n), \quad (88)$$

$$\begin{aligned}
\left\langle \beta^2 \frac{\partial E_{\text{eff}}}{\partial \beta} \right\rangle &= \langle \text{tr} \ln (1 - \delta v_0 F) \rangle - \beta \langle E_{\text{dyn}} \rangle \\
&\quad + \left\langle \beta \left[\frac{\partial (\beta E_{\text{dyn}})}{\partial \beta} \right]_{\omega\Sigma} \right\rangle. \quad (89)
\end{aligned}$$

The first term at the r.h.s. of eq. (87) (*i.e.* eq. (88)) is the contribution from the coherent free energy and reduces to the entropy S_0 for noninteracting electrons when $\Sigma_{L\sigma} \rightarrow 0$:

$$\begin{aligned}
S_0 &= -2 \int d\omega \rho^0(\omega) [f(\omega) \ln f(\omega) \\
&\quad + (1 - f(\omega)) \ln (1 - f(\omega))] , \quad (90)
\end{aligned}$$

where $\rho^0(\omega)$ is the total density of states per spin for noninteracting electrons, $f(\omega)$ is the Fermi distribution function. The second term in eq. (87) (*i.e.* eq. (89)) is the entropy due to the temperature dependence of the effective potential. $[\partial(\beta E_{\text{dyn}})/\partial \beta]_{\omega\Sigma}$ in eq. (89) means to take the derivative with respect to β fixing the frequency

$i\omega_n$ and the coherent potential $\Sigma_{L\sigma}(i\omega_n)$. It is given in the HA as

$$\beta \left[\frac{\partial (\beta E_{\text{dyn}})}{\partial \beta} \right]_{\omega\Sigma} = \frac{\sum_{\nu=1}^{\infty} \sum_{n=1}^{\infty} n \bar{D}_\nu^{(n)}}{1 + \sum_{\nu=1}^{\infty} (\bar{D}_\nu - 1)}. \quad (91)$$

The third and fourth terms in eq. (87) produce the magnetic entropy due to thermal spin fluctuations.

The thermodynamic energy is obtained from the relation $\langle H - \mu N \rangle = \mathcal{F}_{\text{CPA}} + \beta^{-1} S$ as

$$\begin{aligned}
\langle H - \mu N \rangle &= \frac{1}{\beta} \sum_n \sum_{L\sigma} i\omega_n F_{L\sigma}(n) \\
&\quad - \frac{1}{4} \left[(U_0 - 2U_1 + J) \sum_m \langle \tilde{n}_L(\boldsymbol{\xi})^2 \rangle \right. \\
&\quad \left. + (2U_1 - J) \langle \tilde{n}_l(\boldsymbol{\xi})^2 \rangle - \sum_\alpha \tilde{J}_\alpha \left(\langle \xi_\alpha^2 \rangle - \frac{2}{\beta \tilde{J}_\alpha} \right) \right] \\
&\quad + \beta^{-1} \left\langle \frac{\sum_{\nu=1}^{\infty} \sum_{n=1}^{\infty} n \bar{D}_\nu^{(n)}}{1 + \sum_{\nu=1}^{\infty} (\bar{D}_\nu - 1)} \right\rangle. \quad (92)
\end{aligned}$$

The first term at the r.h.s. of eq. (92) is the coherent contribution of the kinetic energy, the second term corresponds to the double counting correction in the Hartree-Fock energy. The last one is the dynamical correction to the energy.

The sum rule $n_0 = \sum_L \langle \tilde{n}_L \rangle$ determines the chemical potential for a given valence electron number n_0 . The CPA equation (73) and effective potential (71) with eqs. (72), (55), and (64) form the self-consistent equations to determine the dynamical coherent potential $\{\Sigma_{L\sigma}(i\omega_n)\}$. After having solved the self-consistent equations, we can calculate the magnetic moments and charge from eqs. (77), (78), and (80), the square of local charge and spin fluctuations from eqs. (83) and (84), as well as the other thermodynamic quantities (see eqs. (70), (87), and (92)).

5. Numerical calculations: Fe and Ni

The simplest approximation to the dynamical CPA is to neglect the dynamical potential $E_{\text{dyn}}(\boldsymbol{\xi})$ in the self-consistent equations. This is called the static approximation and may be justified in the high temperature limit. The next approximation is to add the dynamical potential $E_{\text{dyn}}(\boldsymbol{\xi})$ by taking into account the higher-order terms $\bar{D}^{(n)}$ ($n \geq 1$) in a series expansion (64). We have taken into account the terms up to the second order ($n \leq 2$) in eq. (64). We call this level of approximation the second-order dynamical CPA. Within the approximation, we have performed numerical calculations for Fe and Ni in order to examine the quantitative aspects of the theory and the dynamical effects on their electronic and magnetic properties.

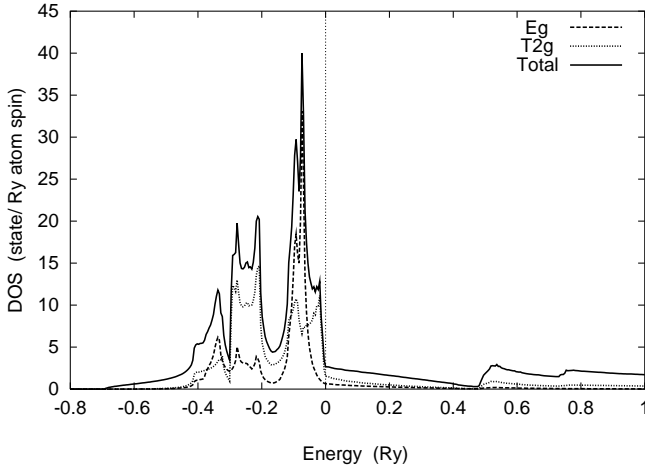


Fig. 1. Densities of states (DOS) calculated by the LDA and TB-LMTO method. Dashed curve: local DOS for e_g electrons, dotted curve: local DOS for t_{2g} electrons, solid curve: total DOS consisting of $4s$, $4p$, and $3d$ orbitals

We obtained the intraorbital Coulomb interaction U_0 , interorbital Coulomb interaction U_1 , and exchange interaction energy parameter J from the parameters \bar{U} and \bar{J} in the LDA + U via the relations: $U_0 = \bar{U} + 8\bar{J}/5$, $U_1 = \bar{U} - 2\bar{J}/5$ and $J = \bar{J}$. (Note that $U_0 = U_1 + 2J$.) We adopted in the present calculations the LDA+U values used by Anisimov *et al.*²⁷; $\bar{U} = 0.1691$ Ry and $\bar{J} = 0.0662$ Ry for Fe, and $\bar{U} = 0.2205$ Ry and $\bar{J} = 0.0662$ Ry for Ni. These values yield $U_0 = 0.2749$ Ry, $U_1 = 0.1426$ Ry, $J = 0.0662$ Ry for Fe, and $U_0 = 0.3263$ Ry, $U_1 = 0.1940$ Ry, and $J = 0.0662$ Ry for Ni, respectively.

In the numerical calculations, we adopted an approximate expression of the coherent Green function³⁶

$$F_{L\sigma}(n) = \int \frac{\rho_L(\epsilon)d\epsilon}{i\omega_n - \epsilon - \Sigma_{L\sigma}(i\omega_n)}. \quad (93)$$

The expression takes into account the effect of hybridization between different l blocks in the nonmagnetic state via the local densities of states $\rho_L(\epsilon)$, but neglects that in the spin polarized state. Moreover, we adopted a decoupling approximation¹³ to the thermal average of the impurity Green function in the dynamical CPA equation (73).

$$\begin{aligned} \langle G_{L\sigma}(n, \xi_z, \xi_z^2) \rangle &= \sum_{q=\pm} \frac{1}{2} \left(1 + q \frac{\langle \xi_z \rangle}{\sqrt{\langle \xi_z^2 \rangle}} \right) \\ &\quad \times G_{L\sigma}(n, q\sqrt{\langle \xi_z^2 \rangle}, \langle \xi_z^2 \rangle). \end{aligned} \quad (94)$$

The approximation is correct up to the second moment and reasonably describe the thermal spin fluctuations. We have solved the dynamical CPA equation for the bcc Fe using the expressions (93) and (94). The densities of states (DOS) for $3d$, $4s$, and $4p$ states were calculated by using von Barth-Hedin LDA potential. The total DOS and the d DOS for e_g and t_{2g} electrons are shown in Fig. 1. Single-particle excitation spectra have been calculated by using the Padé numerical analytic contribution.

Figure 2 shows the calculated d DOS of paramagnetic

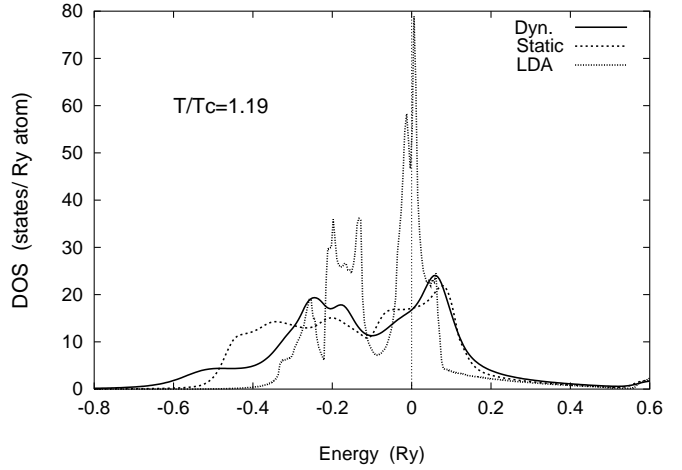


Fig. 2. Single particle excitation spectra (DOS) for d electrons in the paramagnetic Fe. Results for the LDA, the static approximation, and the 2nd-order dynamical CPA are shown by the dotted curve, the dashed curve, and the solid curve, respectively.

Fe at $T/T_C = 1.19$ as the single-particle excitation spectra. The DOS in the static approximation is broadened as compared with the LDA result in the nonmagnetic state because of the strong thermal spin fluctuations. The dynamical charge and spin fluctuations produce a satellite peak around $\omega = -0.5$ Ry ($= -6.8$ eV), and suppress the band broadening by about 22% as compared with the static one. The existence of the satellite peak is consistent with the previous results of the ground-state calculations³⁷ as well as those at finite temperatures.²⁹ The d band width in the present calculations, though it is strongly reduced as compared with the static one, is comparable to that of the LDA calculations, while the XPS experiments suggest the 10% reduction of the width as compared with the LDA results, and no dip at $\omega = -0.1$ Ry.⁵ These inconsistencies may be attributed to an overestimate of the local exchange splitting above T_C .

Below the Curie temperature, the up and down DOS are split as shown in Fig. 3. In the up-spin band, the satellite peak at $\omega = -0.45$ Ry remains, and the quasiparticle bands at $\omega \approx -0.2$ Ry shifts to the Fermi level as compared with those in the static approximation, showing the band narrowing. The satellite peak for the down-spin band disappears because of a large value of $|\text{Im}\Sigma_{L\sigma}(z)|$ in this energy region. These behaviors are consistent with recent QMC calculations without transverse spin fluctuations.²⁹

It is not easy to calculate the DOS at low temperatures in the QMC calculations. The present approach allows us to investigate the DOS even at low temperatures. Figure 4 shows the DOS at $T/T_C = 0.3$. The DOS in the static approximation approaches to the Hartree-Fock one with decreasing temperature, but are still broadened at this temperature by thermal spin fluctuations. Dynamical terms suppress the thermal spin fluctuations and develops the quasiparticle states, so that sharp peaks of e_g electrons appear at $\omega = \pm 0.15$ Ry in the DOS. The present calculations reduce to the 2nd-order perturbation theory at $T = 0$, so that the DOS in Fig. 4 is close

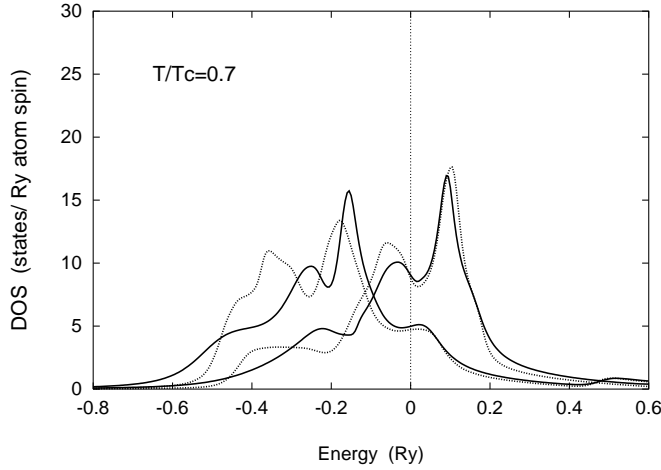


Fig. 3. Up and down d DOS in the ferromagnetic Fe at $T/T_C = 0.7$. Results for the static approximation are shown by the dotted curves.

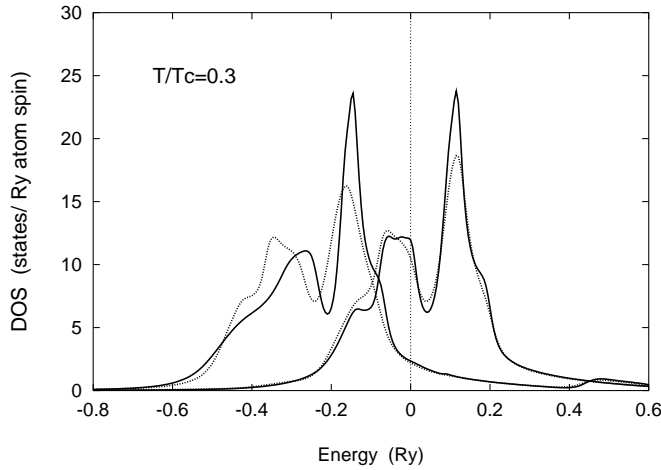


Fig. 4. Up and down d DOS in the ferromagnetic Fe at $T/T_C = 0.3$.

to those obtained at the zero temperature by Drchal *et al.*³⁸

The effective potential determines the behavior of magnetic moments. Figure 5 shows the potential for Fe below T_C . It has double minima along z axis, and monotonically increases with increasing $\xi_{\perp} = \sqrt{\xi_x^2 + \xi_y^2}$. (Note that the effective potential is spherical on the xy plane: $E_{\text{eff}}(\xi_z, \xi_{\perp})$). The dynamical contribution $E_{\text{dyn}}(\xi)$ to the effective potential is given in Fig. 6. The dynamical part shows a 'butterfly' structure; it increases along the z axis with increasing the amplitude $|\xi|$, while it decreases on the xy plane. This implies that the dynamical effects reduce the longitudinal amplitude of spin fluctuations, and enhance the transverse spin fluctuations. In fact, we find 6% reduction of $\sqrt{\langle \xi_z^2 \rangle}$ and 6% enhancement of $\sqrt{\langle \xi_{\perp}^2 \rangle}$ at $T/T_C = 1.19$.

Magnetic properties of Fe are summarized in Fig. 7. Both static and dynamical calculations yield the Curie-Weiss susceptibility. Calculated effective Bohr magneton numbers are $3.1 \mu_B$ in the static approximation and 3.0

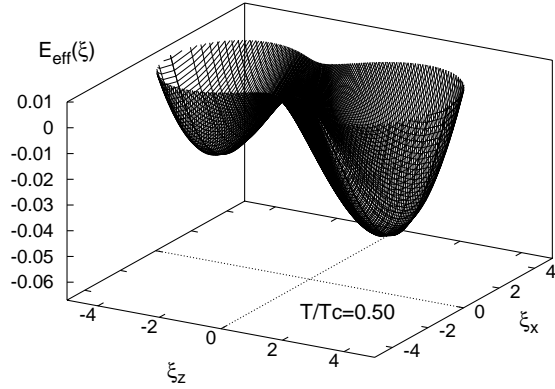


Fig. 5. Effective potential in the ferromagnetic Fe at $T/T_C = 0.5$ on the ξ_x - ξ_z plane.

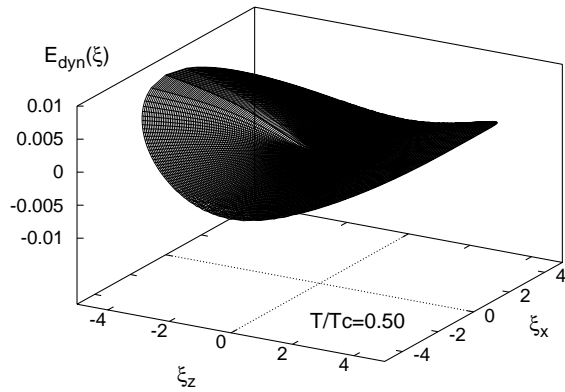


Fig. 6. Dynamical contribution to effective potential in the ferromagnetic Fe at $T/T_C = 0.5$ on the ξ_x - ξ_z plane.

μ_B in the dynamical calculations, respectively, being in good agreement with the experimental value $3.2 \mu_B$.³⁹ Calculated Curie temperature is 2020 K (2070 K) in the 2nd-order dynamical calculations (the static approximation). They are much smaller than the Hartree-Fock value 12200 K, but still twice as large as the experimental value (1040 K).⁴⁰ The present results are comparable to the QMC result of calculations without transverse spin fluctuations (1900 K).²⁹ The reduction of T_C due to dynamical corrections is 50 K, which is rather small. Dynamical effects in general reduce the magnetic energy, but also reduce the magnetic entropy of the static approximation. Both effects are competitive to each other, resulting in the reduction of T_C by 50 K in the case of Fe.

The magnetization increases with decreasing temperature, and reach the Hartree-Fock value $2.61 \mu_B$ at $T = 0$ K in the static approximation. The latter is overestimated as compared with the experimental value $2.216 \mu_B$.⁴¹ The 2nd-order dynamical CPA calculations yield $M = 2.59 \mu_B$ (extrapolated value); the calculations

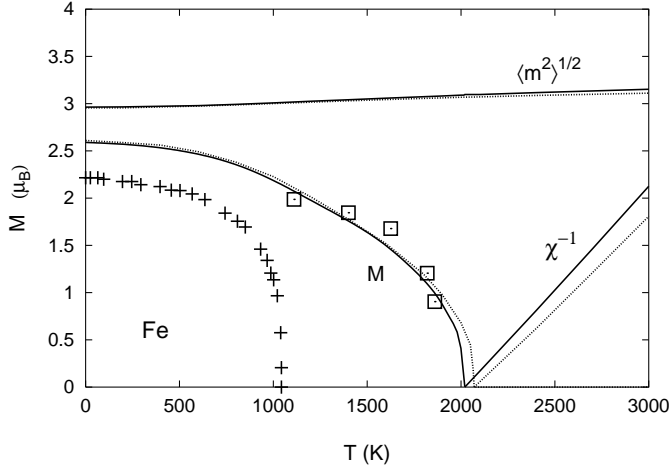


Fig. 7. Calculated magnetization (M), inverse susceptibility (χ^{-1}), and amplitude of local moment ($\langle \mathbf{m}^2 \rangle^{1/2}$) as a function of temperature (T) in Fe. The dynamical results are shown by the solid curves. Results in the static approximation are shown by dotted curves. Magnetization calculated by the DMFT without transverse spin fluctuations²⁹ is also shown by open squares. Experimental data of magnetization⁴² are shown by +. Note that the absolute values of the DMFT magnetization are not given in Ref. 29. Thus they are plotted here by assuming that the extrapolated value at $T = 0$ agrees with the experimental one.

hardly reduce the ground-state magnetization as seen in Fig. 7. One has to take into account the higher-order electron-electron scattering effects as found in the low-density approximation¹⁶ to reduce the magnetization. The amplitude of local magnetic moment was calculated by means of eq. (84). The results are plotted in the same figure. Because of the strong Coulomb interaction, it hardly changes with increasing temperature. The dynamical fluctuations enhance the amplitude $\sqrt{\langle \hat{\mathbf{m}}^2 \rangle}$ by 1%, and reduce the d charge fluctuations $\sqrt{\langle (\delta \hat{n}_d)^2 \rangle}$ by 5% at $T/T_C = 1.2$.

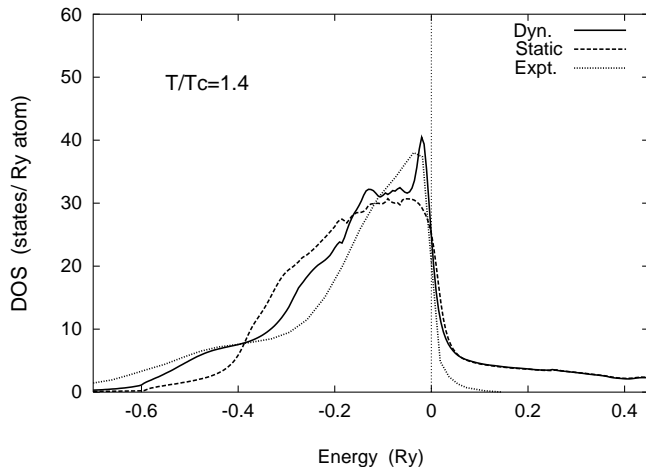


Fig. 8. Calculated DOS in the paramagnetic Ni. Solid curve: 2nd-order dynamical CPA, dashed curve: static approximation, dotted curve: XPS data.⁸

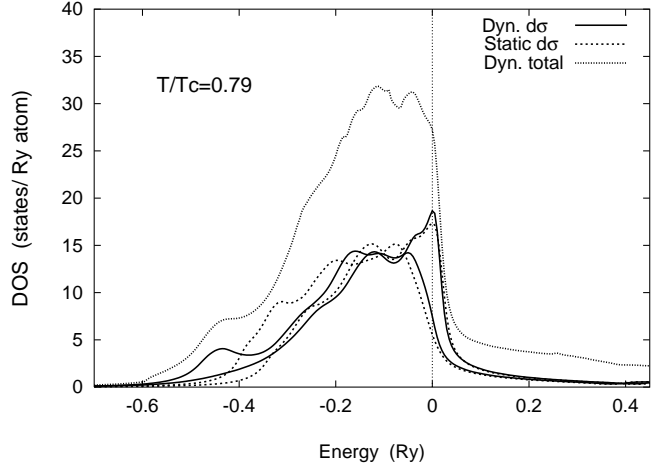


Fig. 9. Calculated DOS in the ferromagnetic Ni. Solid curves : spin-polarized d DOS in the 2nd-order dynamical CPA, dashed curves : spin-polarized d DOS in the static approximation, and dotted curve: total DOS in the 2nd-order dynamical CPA.

We have also calculated the electronic and magnetic properties of the fcc Ni at finite temperatures. Figure 8 shows the DOS in the paramagnetic state. In the static approximation, the details of the structure are smeared by thermal spin fluctuations and the d band width is broadened by about 0.1 Ry. The dynamical effects suppress the thermal spin fluctuations and develop the quasiparticle states. Reduction of the quasiparticle band width is 17% as compared with that of the static approximation. Furthermore we find the satellite peak at $\omega = -0.45$ Ry. These results explain well the XPS data⁸ as shown in Fig. 8.

Below T_C , the peak of the down-spin band is on the Fermi level, as shown in Fig. 9. On the other hand, the top of the up-spin d band is away from the Fermi level, so that the peak is weakened due to larger damping of the quasiparticle states. The satellite peak for the down-spin band disappears due to strong incoherent scatterings around $\omega = -0.35$ Ry, while the satellite peak for the up-spin band is enhanced at $\omega = -0.45$ Ry.

The effective potential for Ni shows a single minimum structure as shown in Fig. 10. The minimum position shifts to the origin with increasing temperature. This should be contrasted to the case of Fe, in which the effective potential has a double minimum structure even above T_C as shown in Fig. 5, and the paramagnetic state is realized by changing the energy difference between the two minima. The dynamical potential $E_{\text{dyn}}(\xi)$ in Ni has a butterfly structure as in the case of Fe, but it is highly asymmetric along the z axis in the ferromagnetic state so that considerable reduction of the magnetization due to dynamical corrections occurs. We find the reduction of $\sqrt{\langle \xi_z^2 \rangle}$ by 5.0%, and the enhancement of $\sqrt{\langle \xi_{\perp}^2 \rangle}$ by 1.5% at $T/T_C = 1.3$.

The magnetic moment and the inverse susceptibility calculated from the effective potential are presented in Fig. 11 as a function of temperature. The susceptibility follows the Curie-Weiss law. Both the static and dynamical calculations yield the effective Bohr magneton

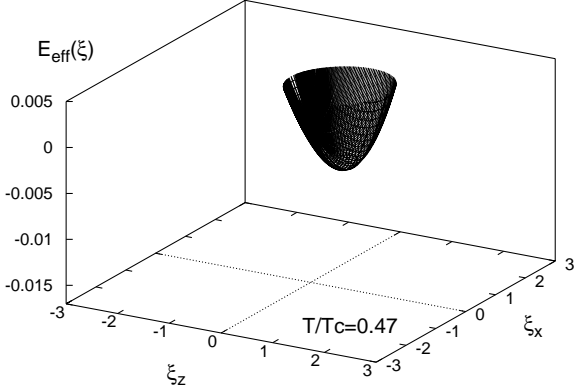


Fig. 10. Effective potential in the ferromagnetic Ni at $T/T_C = 0.47$ on the ξ_x - ξ_z plane.

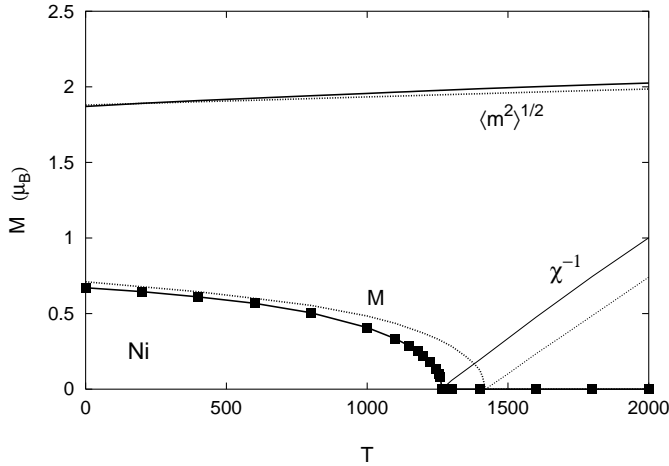


Fig. 11. Magnetization, inverse susceptibility, and amplitude of local moment as a function of temperature in Ni. The dynamical results are shown by the solid curves, while the results in the static calculation are shown by dotted curves.

number $1.2 \mu_B$, which should be compared with the experimental value $1.6 \mu_B$.⁴³ Calculated Curie temperature in Ni is 1260 K (1420 K) in the 2nd-order dynamical (static) calculations. These values are much smaller than the Hartree-Fock value 4950 K, but are still twice as large as the experimental value 630 K.⁴⁰

The magnetization increases with decreasing temperature below T_C . Extrapolated value at $T = 0$ is 0.67 (0.71) μ_B in the 2nd-order dynamical (static) calculations. These values are considerably larger than the experimental one ($0.62 \mu_B$).⁴¹ The amplitude of Ni local moment slightly increases with increasing temperature and hardly shows anomaly at T_C . The 2nd order dynamical corrections to the amplitude of local moment and the local charge fluctuations are small; the enhancement of $\sqrt{\langle \hat{m}^2 \rangle}$ is only 1.8 % and the reduction of the d charge fluctuations $\sqrt{\langle (\delta \hat{n}_d)^2 \rangle}$ is 5.9 % at $T/T_C = 1.3$.

6. Summary

We have developed the dynamical CPA on the basis of the LDA+TB-LMTO Hamiltonian towards realistic calculations of the itinerant electron system. The theory is a direct extension of the single-site theory developed by Cyrot, Hubbard, Hasegawa, and Kakehashi, to the degenerate band case. It is based on the functional integral method which transforms the interacting electron system into an independent electron system with time-dependent random charge and exchange potentials. Using the method, we have taken into account the spin fluctuations as well as charge fluctuations in the degenerate band system. We have then introduced an effective medium $\Sigma_{L\sigma}(i\omega_n)$, and derived the self-consistent dynamical CPA equation for the medium, making use of a single-site approximation.

We adopted the harmonic approximation (HA) to treat the functional integrals in the dynamical CPA. The HA describes the dynamical effects from the weak- to the strong- Coulomb interaction regime. The approximation allows us to obtain analytical expressions of the physical quantities, and takes into account the dynamical corrections successively starting from a high-temperature approximation (*i.e.*, the static approximation). We can calculate the excitation spectra as well as the thermodynamic quantities even at low temperatures using the HA because we obtained their analytic expressions.

We have investigated the dynamical effects in Fe and Ni within the 2nd-order dynamical CPA, and have shown that the 2nd-order dynamical corrections much improve the single-particle excitation spectra in these systems. The static approximation broadens the DOS due to thermal spin fluctuations at finite temperatures. The dynamical effects suppress the thermal spin fluctuations and create the quasiparticle states with narrow band width near the Fermi level. Furthermore, the correlations create the satellite peak at 6 eV below the Fermi level in both Fe and Ni. The XPS data in the paramagnetic Ni is well explained by the present theory.

We verified that the dynamical CPA yields the Curie-Weiss susceptibilities. Calculated effective Bohr magneton numbers, $3.0 \mu_B$ for Fe and $1.2 \mu_B$ for Ni, explain the experimental data quantitatively or semiquantitatively. Calculated Curie temperatures, 2020 K for Fe and 1260 K for Ni, are however overestimated by a factor of two. Extrapolated values of the ground state magnetization, $2.59 \mu_B$ for Fe and $0.67 \mu_B$ for Ni, are also overestimated considerably as compared with the experimental ones ($2.22 \mu_B$ for Fe and $0.62 \mu_B$ for Ni).

We found that the static approximation provides us with a good starting point to calculate finite-temperature magnetic properties of Fe and Ni, but the dynamical calculations to go beyond the static approximation have been limited to the second-order dynamical CPA in the present work. Overestimate of the ground-state magnetization and the Curie temperature should be reduced by taking into account the higher-order dynamical fluctuations. Further improvements of the dynamical CPA theory are left for future investigations.

Acknowledgment

We would like to express our sincere thanks to Dr. Ove Jepsen for sending us the Stuttgart TB-LMTO program and fruitful advice on how to install the program on our computer.

Appendix A: Expression of $\hat{D}_{\{\alpha\gamma\}}^{(n)}(\nu, k, m)$

We calculate in this appendix the coefficients $\hat{D}_{\{\alpha\gamma\}}^{(n)}(\nu, k, m)$ in the n -th order expansion of the determinant $D_\nu(k, m)$ with respect to the dynamical potential $v_\alpha(\nu, m)$.

Let us rewrite $D_\nu(k, m)$ defined by eq. (57) as follows by making use of the Laplace expansion.

$$D = |a^{(0)}| \bar{D}_{20} D_{20} + \sum_{\alpha\gamma} (a^{(0)})_{\alpha\gamma} \Delta_{\gamma\alpha} + \bar{D}_{10} D_{10}, \quad (\text{A.1})$$

$$\Delta_{11} = -(\bar{D}_{20} - \bar{D}_{24})(D_{20} - D_{24}) - \bar{D}_{23} D_{23}, \quad (\text{A.2})$$

$$\Delta_{12} = -\bar{D}_{23}(D_{20} - D_{21}) - (\bar{D}_{20} - \bar{D}_{24}) D_{22}, \quad (\text{A.3})$$

$$\Delta_{21} = -\bar{D}_{22}(D_{20} - D_{24}) - (\bar{D}_{20} - \bar{D}_{21}) D_{23}, \quad (\text{A.4})$$

$$\Delta_{22} = -(\bar{D}_{20} - \bar{D}_{21})(D_{20} - D_{21}) - \bar{D}_{22} D_{22}. \quad (\text{A.5})$$

In the above equations, we have omitted the suffixes ν, k, m for simplicity, and $|a^{(0)}|$ denotes the determinant of the 2×2 matrix $a_k(\nu, m)$. $\{D_{n\alpha}\}$ at the r.h.s. of eqs. (A.1-A.5) are defined by

$$D_{n\alpha} = \begin{vmatrix} b_\alpha^{(n-1)} & 1 & & 0 \\ a_\alpha^{(n)} & 1 & 1 & \\ & a^{(n+1)} & 1 & 1 \\ & & & \ddots \\ 0 & & & \end{vmatrix}, \quad (\text{A.6})$$

$$\bar{D}_{n\alpha} = \begin{vmatrix} \bar{b}_\alpha^{(n-1)} & \bar{a}_\alpha^{(n)} & & 0 \\ 1 & 1 & \bar{a}^{(n+1)} & \\ & 1 & 1 & \bar{a}^{(n+2)} \\ & & & \ddots \\ 0 & & & \end{vmatrix}. \quad (\text{A.7})$$

Here $a^{(n)}$ ($\bar{a}^{(n)}$) stands for $a_{n\nu+k}(\nu, m)$ ($a_{-n\nu+k}(\nu, m)$). $a_\alpha^{(n)}$, $b_\alpha^{(n)}$, $\bar{a}_\alpha^{(n)}$, and $\bar{b}_\alpha^{(n)}$ are defined by $a_0^{(n)} = a^{(n)}$, $b_0^{(n)} = 1$, $\bar{a}_0^{(n)} = a^{(-n)}$, $\bar{b}_0^{(n)} = 1$, and for $\alpha = 1 \sim 4$,

$$a_1^{(n)} = a_2^{(n)} = \begin{pmatrix} 0 & a_{12}^{(n)} \\ 0 & a_{22}^{(n)} \end{pmatrix}, a_3^{(n)} = a_4^{(n)} = \begin{pmatrix} 0 & a_{11}^{(n)} \\ 0 & a_{21}^{(n)} \end{pmatrix}, \quad (\text{A.8})$$

$$b_1^{(n)} = \begin{pmatrix} a_{11}^{(n)} & 0 \\ a_{21}^{(n)} & 1 \end{pmatrix}, b_2^{(n)} = \begin{pmatrix} a_{12}^{(n)} & 0 \\ a_{22}^{(n)} & 1 \end{pmatrix},$$

$$b_3^{(n)} = \begin{pmatrix} a_{11}^{(n)} & 1 \\ a_{21}^{(n)} & 0 \end{pmatrix}, b_4^{(n)} = \begin{pmatrix} a_{12}^{(n)} & 1 \\ a_{22}^{(n)} & 0 \end{pmatrix}, \quad (\text{A.9})$$

$$\bar{a}_1^{(n)} = \bar{a}_2^{(n)} = \begin{pmatrix} 0 & 0 \\ a_{21}^{(-n)} & a_{22}^{(-n)} \end{pmatrix},$$

$$\bar{a}_3^{(n)} = \bar{a}_4^{(n)} = \begin{pmatrix} 0 & 0 \\ a_{11}^{(-n)} & a_{12}^{(-n)} \end{pmatrix}, \quad (\text{A.10})$$

$$\bar{b}_1^{(n)} = \begin{pmatrix} a_{11}^{(-n)} a_{12}^{(-n)} \\ 0 & 1 \end{pmatrix}, \bar{b}_2^{(n)} = \begin{pmatrix} a_{21}^{(-n)} a_{22}^{(-n)} \\ 0 & 1 \end{pmatrix},$$

$$\bar{b}_3^{(n)} = \begin{pmatrix} a_{11}^{(-n)} a_{12}^{(-n)} \\ 1 & 0 \end{pmatrix}, \bar{b}_4^{(n)} = \begin{pmatrix} a_{21}^{(-n)} a_{22}^{(-n)} \\ 1 & 0 \end{pmatrix}. \quad (\text{A.11})$$

It should be noted that eq. (A.1) is calculated from a set $(D_{10}, D_{20}, D_{21}, D_{22}, D_{23}, D_{24})$. Thus we define $\mathbf{D}^{(n)}$ by ${}^t\mathbf{D}^{(n)} = (D_{n0}, D_{n+10}, D_{n+11}, D_{n+12}, D_{n+13}, D_{n+14})$. By making use of the Laplace expansion, we can derive a recursion relation as follows.

$$\mathbf{D}^{(n)} = (c_0 + c_1^{(n)} + c_2^{(n)}) \mathbf{D}^{(n+2)}. \quad (\text{A.12})$$

Here $(c_0)_{ij} = \delta_{i1}\delta_{j1} + \delta_{i2}\delta_{j1}$, and

$$c_1^{(n)} = \begin{pmatrix} -a_{11}^{(n)} - a_{22}^{(n)} - a_{11}^{(n+1)} a_{22}^{(n+1)} & a_{22}^{(n+1)} - a_{21}^{(n+1)} - a_{12}^{(n+1)} a_{11}^{(n+1)} \\ 0 & -a_{11}^{(n+1)} a_{22}^{(n+1)} - a_{22}^{(n+1)} - a_{21}^{(n+1)} - a_{12}^{(n+1)} a_{11}^{(n+1)} \\ a_{11}^{(n)} & 0 & 0 & 0 & 0 & 0 \\ a_{12}^{(n)} & 0 & 0 & 0 & 0 & 0 \\ a_{21}^{(n)} & 0 & 0 & 0 & 0 & 0 \\ a_{22}^{(n)} & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (\text{A.13})$$

$$c_2^{(n)} = \begin{pmatrix} a^{(n)} | c_{12}^{(n,n+1)} - c_{11221221}^{(n,n+1)} c_{22212122}^{(n,n+1)} c_{11121211}^{(n,n+1)} - c_{22112112}^{(n,n+1)} \\ 0 | a^{(n+1)} | 0 & 0 & 0 & 0 \\ 0 - c_{11222112}^{(n,n+1)} a_{11}^{(n)} a_{22}^{(n+1)} a_{21}^{(n)} a_{22}^{(n+1)} - a_{11}^{(n)} a_{12}^{(n+1)} - a_{21}^{(n)} a_{12}^{(n+1)} \\ 0 c_{22121222}^{(n,n+1)} a_{12}^{(n)} a_{22}^{(n+1)} a_{22}^{(n)} a_{22}^{(n+1)} - a_{12}^{(n)} a_{12}^{(n+1)} - a_{22}^{(n)} a_{12}^{(n+1)} \\ 0 c_{11212111}^{(n,n+1)} - a_{11}^{(n)} a_{21}^{(n+1)} - a_{21}^{(n)} a_{11}^{(n+1)} a_{11}^{(n)} a_{11}^{(n+1)} a_{21}^{(n)} a_{11}^{(n+1)} \\ 0 - c_{22111221}^{(n,n+1)} - a_{12}^{(n)} a_{21}^{(n+1)} - a_{22}^{(n)} a_{21}^{(n+1)} a_{12}^{(n)} a_{11}^{(n+1)} a_{22}^{(n)} a_{11}^{(n+1)} \end{pmatrix}. \quad (\text{A.14})$$

Here $c_{\alpha\beta\gamma\delta\alpha'\beta'\gamma'\delta'}^{(n,n+1)} = a_{\alpha\beta}^{(n)} a_{\gamma\delta}^{(n+1)} - a_{\alpha'\beta'}^{(n)} a_{\gamma'\delta'}^{(n+1)}$, and $c_{12}^{(n,n+1)} = c_{11221221}^{(n,n+1)} + c_{22112112}^{(n,n+1)} + |a^{(n+1)}|$. Note that c_0 , $c_1^{(n)}$, and $c_2^{(n)}$ matrices are of the 0-th order, the first order, and the second order with respect to the dynamical potential v , respectively.

Using the relation $c_0^2 = c_0$ and $D_{\infty 0} = 1$, we obtain the relation.

$$\mathbf{D}^{(m)} = \mathbf{E}_2 + \sum_{n=0}^{\infty} c_0^n (\mathbf{D}^{(m+2n)} - c_0 \mathbf{D}^{(m+2n+2)}). \quad (\text{A.15})$$

Here ${}^t\mathbf{E}_2 = (1, 1, 0, 0, 0, 0)$.

Substituting eq. (A.12) into eq. (A.15), and using the recursion relation successively, we reach the expansion of $\mathbf{D}^{(1)}$ with respect to the dynamical potential v .

$$\mathbf{D}^{(1)} = \mathbf{E}_2 + \sum_{n=1}^{\infty} \sum_{k \geq n} \sum_{2l_k=0}^n \sum_{l_{k-1}=0}^{\infty} \sum_{l_1=0}^{\infty} \sum_{i_1+\dots+i_k=n} c_0^{l_1} c_{i_1}^{2l_1+1} \cdot c_0^{l_{k-1}} c_{i_{k-1}}^{2l_{k-1}+1} \cdot c_0^{l_k} c_{i_k}^{2l_k+1} \mathbf{E}_2, \quad (\text{A.16})$$

where $i_1 \cdots i_k$ take a value 1 or 2.

In the same way, we obtain the expansion of $\overline{D}^{(1)}$ as

$$\overline{D}^{(1)} = \mathbf{E}_2 + \sum_{n=1}^{\infty} \sum_{k \geq n/2} \sum_{l_k=0}^{\infty} \sum_{l_{k-1}=0}^{l_k} \cdots \sum_{l_1=0}^{l_2} c_0^{l_1} \bar{c}_{i_1}^{2l_1+1} \cdots c_0^{l_{k-1}} \bar{c}_{i_k}^{2l_{k-1}+2k-1} \mathbf{E}_2. \quad (\text{A}\cdot 17)$$

Here $\bar{c}_1^{(n)}$ and $\bar{c}_2^{(n)}$ are defined by c_1 and c_2 in which $\{a^{(n)}\}$ have been replaced by $\{\bar{a}^{(n)}\}$.

Substituting eqs. (A.16) and (A.17) into eq. (A.1), we obtain the expansion of D with respect to dynamical potentials.

$$D_{\nu}^{(n)}(k, m) = \sum_{n=0}^{\infty} \sum_{\alpha_1 \gamma_1 \cdots \alpha_n \gamma_n} v_{\alpha_1}(\nu, m) v_{\gamma_1}(-\nu, m) \cdots \\ \times v_{\alpha_n}(\nu, m) v_{\gamma_n}(-\nu, m) \hat{D}_{\{\alpha \gamma\}}^{(n)}(\nu, k, m). \quad (\text{A}\cdot 18)$$

Note that α_n and γ_n take 0, x , y , and z .

The first few terms of $\hat{D}_{\{\alpha \gamma\}}^{(n)}(\nu, k, m)$ are expressed as follows.

$$\hat{D}^{(0)}(\nu, k, m) = 1, \quad (\text{A}\cdot 19)$$

$$\hat{D}_{\alpha \gamma}^{(1)}(\nu, k, m) = - \sum_{n=-\infty}^{\infty} \sum_{\sigma} \hat{a}_{\alpha \gamma}(\nu, m, n\nu + k)_{\sigma \sigma}, \quad (\text{A}\cdot 20)$$

$$\hat{D}_{\alpha \gamma \alpha' \gamma'}^{(2)}(\nu, k, m) = \frac{1}{2} \hat{D}_{\alpha \gamma}^{(1)}(\nu, k, m) \hat{D}_{\alpha' \gamma'}^{(1)}(\nu, k, m) \\ - \frac{1}{2} \sum_{n=-\infty}^{\infty} \left(\sum_{\sigma} \hat{a}_{\alpha \gamma}(\nu, m, n\nu + k)_{\sigma \sigma} \right) \left(\sum_{\sigma} \hat{a}_{\alpha' \gamma'}(\nu, m, n\nu + k)_{\sigma \sigma} \right) \\ + \sum_{n=-\infty}^{\infty} \left[\hat{a}_{\alpha \gamma}(\nu, m, n\nu + k)_{\uparrow \uparrow} \hat{a}_{\alpha' \gamma'}(\nu, m, n\nu + k)_{\downarrow \downarrow} \right. \\ \left. - \hat{a}_{\alpha \gamma}(\nu, m, n\nu + k)_{\downarrow \uparrow} \hat{a}_{\alpha' \gamma'}(\nu, m, n\nu + k)_{\uparrow \downarrow} \right. \\ \left. - \sum_{\sigma \sigma'} \hat{a}_{\alpha \gamma}(\nu, m, n\nu + k)_{\sigma \sigma'} \hat{a}_{\alpha' \gamma'}(\nu, m, n\nu + k)_{\sigma' \sigma} \right]. \quad (\text{A}\cdot 21)$$

Here $\hat{a}_{\alpha \gamma}(\nu, m, n)$ is defined by

$$\hat{a}_{\alpha \gamma}(\nu, m, n) = \left[(1 + O_1 \sigma_x + O_2 \sigma_y + O_3 \sigma_z) \bar{h}(m, n - \nu, n) \right]_{\alpha \gamma}. \quad (\text{A}\cdot 22)$$

O_1, O_2, O_3 , and \bar{h} in eq. (A.22) are 4×4 matrices defined by

$$O_1 = \begin{pmatrix} \sigma_x & 0 \\ 0 & -\sigma_y \end{pmatrix}, \quad O_2 = \begin{pmatrix} 0 & \lambda^* + \lambda \sigma_z \\ \lambda + \lambda^* \sigma_z & 0 \end{pmatrix}, \\ O_3 = \begin{pmatrix} 0 & \lambda(\sigma_x + \sigma_y) \\ \lambda^*(\sigma_x + \sigma_y) & 0 \end{pmatrix}, \quad (\text{A}\cdot 23)$$

$$\bar{h}(m, n - \nu, n) = \begin{pmatrix} e_0 + e_x + e_y + e_z & a_x^{(+)} - ib_x^{(-)} & a_y^{(+)} - ib_y^{(-)} & a_z^{(+)} - ib_z^{(-)} \\ a_x^{(+)} + ib_x^{(-)} & e_0 + e_x - e_y - e_z & b_z^{(+)} - ia_z^{(-)} & b_y^{(+)} + ia_y^{(-)} \\ a_y^{(+)} + ib_y^{(-)} & b_z^{(+)} + ia_z^{(-)} & e_0 - e_x + e_y - e_z & b_x^{(+)} - ia_x^{(-)} \\ a_z^{(+)} + ib_z^{(-)} & b_y^{(+)} - ia_y^{(-)} & b_x^{(+)} + ia_x^{(-)} & e_0 - e_x - e_y + e_z \end{pmatrix}. \quad (\text{A}\cdot 24)$$

Here $\lambda = (1 + i)/2$, and

$$e_{\alpha} = g_L^{\alpha}(n - \nu) g_L^{\alpha}(n) \quad (\alpha = 0, x, y, z), \quad (\text{A}\cdot 25)$$

$$a_{\alpha}^{(\pm)} = g_L^{\alpha}(n - \nu) g_L^0(n) \pm g_L^0(n - \nu) g_L^{\alpha}(n) \quad (\alpha = x, y, z), \quad (\text{A}\cdot 26)$$

$$b_{\alpha}^{(\pm)} = g_L^{\beta}(n - \nu) g_L^{\gamma}(n) \pm g_L^{\gamma}(n - \nu) g_L^{\beta}(n) \quad (\alpha = x, y, z). \quad (\text{A}\cdot 27)$$

Note that (α, β, γ) in eq. (A.27) denotes a cyclic change of (x, y, z) . The static Green functions $g_L^{\alpha}(n)$ ($\alpha = 0, x, y, z$) are defined by $\tilde{g}_{L\sigma\sigma'}(n)$ (see eq. (51)) as

$$\tilde{g}_{L\sigma\sigma'}(n) = g_L^0(n) \delta_{\sigma\sigma'} + \sum_{\alpha}^{x,y,z} g_L^{\alpha}(n) (\sigma_{\alpha})_{\sigma\sigma'}. \quad (\text{A}\cdot 28)$$

Appendix B: Calculation of the Gaussian average of dynamical potentials

We calculate here the Gaussian average of the n -th order products of dynamical potentials.

$$\overline{\left[\prod_{m=1}^{2l+1} \prod_{k=1}^{n(m)} (v_{\alpha_k(m)}(\nu, m) v_{\gamma_k(m)}(-\nu, m)) \right]} = \\ \int \left[\prod_{\alpha}^{xyz} \frac{\beta^{2l+1} \det B^{\alpha}}{(2\pi)^{2l+1}} \prod_{m=1}^{2l+1} d^2 \xi_{m\alpha}(\nu) \right] \frac{\beta^{2l+1} \det A}{(2\pi)^{2l+1}} \left[\prod_{m=1}^{2l+1} d^2 \zeta_m(\nu) \right] \\ \times \left[\prod_{m=1}^{2l+1} \left(\prod_{k=1}^{n(m)} v_{\alpha_k(m)}(\nu, m) v_{\gamma_k(m)}(-\nu, m) \right) \right] \\ \times \exp \left[-\frac{\beta}{2} \left(\zeta^*(\nu) A \zeta(\nu) + \sum_{\alpha} \xi_{\alpha}^*(\nu) B^{\alpha} \xi_{\alpha}(\nu) \right) \right]. \quad (\text{B}\cdot 1)$$

Here integers $\{n(m)\}$ satisfy the constraint $\sum_m n(m) = n$. $\zeta^*(\nu) A \zeta(\nu)$ stands for $\sum_{mm'} \zeta_m^*(\nu) A_{mm'} \zeta_{m'}(\nu)$. $v_{\alpha}(\nu, m)$ are given by eqs. (61) and (62).

The average is calculated from a generating function $I(s, t)$ as follows.

$$\overline{\left[\prod_{m=1}^{2l+1} \prod_{k=1}^{n(m)} (v_{\alpha_k(m)}(\nu, m) v_{\gamma_k(m)}(-\nu, m)) \right]} = \left[\prod_{m=1}^{2l+1} \frac{\partial^{2n(m)}}{\partial s_{m\alpha_1(m)} \partial t_{m\gamma_1(m)} \cdots \partial s_{m\alpha_{n(m)}(m)} \partial t_{m\gamma_{n(m)}(m)}} \right] I(s=0, t=0). \quad (\text{B}\cdot 2)$$

Here

$$I(s, t) = \int \left[\prod_{\alpha}^{xyz} \frac{\beta^{2l+1} \det B^{\alpha}}{(2\pi)^{2l+1}} \prod_{m=1}^{2l+1} d^2 \xi_{m\alpha}(\nu) \right] \frac{\beta^{2l+1} \det A}{(2\pi)^{2l+1}} \left[\prod_{m=1}^{2l+1} d^2 \zeta_m(\nu) \right] \\ \times \exp \left[-\frac{\beta}{2} \left(\zeta^*(\nu) A \zeta(\nu) + \sum_{\alpha} \xi_{\alpha}^*(\nu) B^{\alpha} \xi_{\alpha}(\nu) \right) \right. \\ \left. + \sum_{m=1}^{2l+1} \sum_{\alpha=0}^4 \left(s_{m\alpha} v_{\alpha}(\nu, m) + t_{m\alpha} v_{\alpha}(-\nu, m) \right) \right]. \quad (\text{B}\cdot 3)$$

The latter is obtained as follows.

$$I(s, t) = \exp \left[\frac{1}{2\beta} \sum_{mm'\alpha} s_{m\alpha} C_{mm'}^\alpha t_{m'\alpha} \right]. \quad (\text{B}\cdot 4)$$

Here the Coulomb interactions $C_{mm'}^\alpha$ are defined by eq. (66).

By differentiating $I(s, t)$ with respect to $s_{m\alpha}$ ($t_{m\gamma}$), we have a new factor $(2\beta)^{-1} \sum_n C_{mn}^\alpha t_{n\alpha}$ ($(2\beta)^{-1} \sum_n s_{n\gamma} C_{nm}^\gamma$). When we take the $2n$ -th derivative of $I(s, t)$ with respect to the variable $(s_{m\alpha_1}, t_{m\gamma_1}, \dots, s_{m\alpha_n}, t_{m\gamma_n})$, we have a $2n$ -th order polynomial times $I(s, t)$. When we put $s_{m\alpha} = 0$ and $t_{m\alpha} = 0$ in the derivative, we have $I(s = 0, t = 0) = 1$, and only the 0-th order terms of the polynomial remain. The latters were created by taking a derivative of the factor $(2\beta)^{-1} \sum_n s_{n\alpha} C_{nm}^\alpha$ or $(2\beta)^{-1} \sum_{n'} C_{mn'}^\gamma t_{n'\gamma}$ with respect to the variable conjugate to $s_{m\gamma_i}$ or $t_{m'\alpha_i}$. A created constant $\frac{(1/2\beta) C_{mm'}^{\alpha_i} \delta_{\alpha_i \gamma_j}}{s_{m\alpha_i} t_{m'\gamma_j}}$ may be indicated by a contraction $\overline{s_{m\alpha_i} t_{m'\gamma_j}}$. Then the 0-th order terms, and therefore the Gaussian average (B-1) should be given by the sum over all possible products of contractions.

$$\overline{\left[\prod_{m=1}^{2l+1} \prod_{k=1}^{n(m)} (v_{\alpha_k(m)}(\nu, m) v_{\gamma_k(m)}(-\nu, m)) \right]} = \frac{1}{(2\beta)^n} \sum_P \left[\prod_{m=1}^{2l+1} \prod_{k=1}^{n(m)} C_{mm_p}^{\alpha_k(m)} \delta_{\alpha_k(m) \gamma_{k_p}(m_p)} \right]. \quad (\text{B}\cdot 5)$$

Here the permutation P is taken with respect to the n elements $\{(k, m) | k = 1, \dots, n(m); m = 1, \dots, 2l+1\}$; $P\{(k, m)\} = \{(k_p, m_p)\}$. Application of the formula (B-5) to eq. (63) yields eq. (65) in §4:

$$\overline{D}_\nu^{(n)} = \frac{1}{(2\beta)^n} \sum_{km} \sum_{l(k,m)=n} \sum_{\{\alpha_j(k,m)\}} \prod_{m=1}^{2l+1} \prod_{k=0}^{\nu-1} \left[\left(\prod_{j=1}^{l(k,m)} C_{mm_p}^{\alpha_j} \right) \hat{D}_{\{\alpha_{p-1}\}}^{(l(k,m))}(\nu, k, m) \right]. \quad (\text{B}\cdot 6)$$

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